

[DOCUMENT NAME] SPECIFICATION
[TITLE OF THE INVENTION]
IMAGE FORMING METHOD USING PHOTOTHERMOGRAPHIC MATERIAL

[WHAT IS CLAIMED IS]

[Claim 1] An image forming method using a photothermographic material comprising a photosensitive silver halide, a reducing agent, a binder and a non-photosensitive organic silver salt, wherein:

the photothermographic material is discharged from a thermal developing device within 35 seconds after heating for thermal development is ceased.

[Claim 2] The method of claim 1, wherein, when the photothermographic material is exposed with an amount of light sufficient to make image density of 1.0 by a thermal development of 14 seconds, thermal development for 16 seconds yields an image density of 1.0 to 1.3.

[Claim 3] The method of claim 1 or 2, wherein the non-photosensitive organic silver salt contains 30 mol% to 100 mol% of silver behenate.

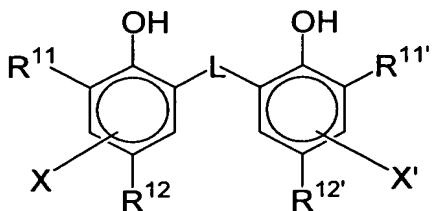
[Claim 4] The method of any one of claims 1 to 3, wherein the photothermographic material includes at least one type of development accelerator.

[Claim 5] The method of any one of claims 1 to 4, wherein the reducing agent is a bisphenol reducing agent.

[Claim 6] The method of claim 5, wherein the reducing agent is a compound represented by the following general formula (R):

General formula (R)

[Formula 1]



wherein R¹¹ and R^{11'} each independently represent one of a secondary and a tertiary alkyl group having 3 to 15 carbon atoms, R¹² and R^{12'} each independently represent a hydrogen atom or a substituent capable of substituting for a hydrogen atom on a benzene ring, L represents one of a -S- group and a -CHR¹³- group, R¹³ represents one of a hydrogen atom and an alkyl group having 1 to 20 carbon atoms, and X¹ and X'¹ each independently represent a hydrogen atom or a substituent capable of substituting for a hydrogen atom on a benzene ring.

[Claim 7] The method of any one of claims 1 to 6, wherein the photothermographic material includes at least one type of phthalazine compound.

[Claim 8] The method of claim 7, wherein the content of the phthalazine compound is 0.01 mol to 10 mol per one mol of applied silver.

[Claim 9] The method of any one of claims 1 to 8, wherein the photothermographic material includes at least one type of mercapto compound.

[Claim 10] The method of any one of claims 1 to 9, wherein the photothermographic material includes at least one type of benzotriazole compound.

[Claim 11] The method of any one of claims 1 to 10, wherein the photothermographic material includes a thermal solvent having a melting point of 50 °C to 200 °C.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field of the Invention]

The present invention relates to a method of forming an image using a light-sensitive thermal developing material (hereinafter occasionally referred to as the “photothermographic material”). More particularly, the present invention relates to a method of forming an image using a photothermographic material that causes little blurring in development.

[0002]

[Prior Art]

Recently, there is a strong demand in the medical field for reduction in the volume of waste processing liquid from the viewpoint of environmental preservation and economy of space. There have been demands for technologies relating to a photothermographic material for medical imaging and graphic arts. In particular, there is a demand for a photothermographic material that is efficiently exposed by a laser image setter or a laser imager, and provides black-toned images with high resolution and sharpness. Such a photothermographic material can provide users with a simpler and ecological thermal developing system without the use of liquid processing chemicals.

[0003]

Although there are similar demands in the field of general image forming materials, high image quality (i.e., excellent sharpness and fine graininess) is required for images used in medical imaging where high image quality of excellent sharpness and granularity is necessary. Further, images with blue-black tones are preferred from the perspective of facilitating diagnosis. Various types of hard copy systems using pigment or dye, such as an inkjet printer and an electrophotographic system, are commonly used as a general image forming system. But none of these is satisfactory as an output system for medical images.

[0004]

In general, thermal image forming systems using organic silver salts are described in, for example, the specifications of patent documents 1 and 2 and a non-patent document 1. A photothermographic material typically includes a photosensitive layer in which a catalytically active amount of a photocatalyst (e.g., silver halide), a reducing agent, reducible silver salt (e.g., organic silver salt) and a toner for controlling the tone of a

developed silver image as needed are dispersed in the matrix of a binder. After an image is exposed thereon, a photothermographic material is heated to a high temperature (e.g., 80 °C or above) to cause an oxidation-reduction reaction between silver halide or reducible silver salt (which acts as an oxidizing agent) and a reducing agent, thus providing a black silver image. The oxidation-reduction reaction is accelerated by the catalytic action of a latent image of the exposed silver halide. Thermal image forming systems are disclosed in many documents including patent documents 3 and 4. Fuji Medical Dry Laser Imager FM-DP L is commercially available as a medical image forming system using a photothermographic material.

[0005]

A thermal image forming system using organic silver salt is manufactured by either a coating method with an organic solvent, or a coating method with a luster solvent, wherein a coating solution containing polymer particles as a main binder is coated and dried. Manufacturing facility for the latter method is simple because a step of recovering a solvent is unnecessary. Further, the latter method is advantageous in terms of mass production.

[0006]

There has always been a demand for improving processing capacity of a thermal developing process for the above-described photothermographic materials. A system using laser light such as a laser imager enables sequential output of images on the photosensitive materials and thus has substantially improved the processing speed. Increasing the processing speed per sheet of photosensitive material is most effective in improving the processing capacity and has been the greatest challenge.

An exposing device and a thermal developing device are incorporated as components of various medical diagnosing systems and image information processing systems and are used in various environments. In order to achieve reduction in size of the entire system, there is a demand for compact laser exposing sections and thermal developing sections as well.

In order to meet these challenges and demands, it is necessary to improve performance of the exposing and developing devices and also improve the photothermographic materials. As described above, in the thermal image forming system using the photothermographic material, a black silver image is formed by activating silver halide by light and causing an oxidation-reduction reaction by heat. Thus, the processing capacity cannot be improved unless a photothermographic material, in which silver halide is sensitive to light even with shorter exposure time and sensitively reacts to light so as to cause an oxidation-reduction reaction, is provided.

Another important problem in improving the processing speed is to develop a photothermographic material adapted to high speed processing. The overall problems facing the thermal processing system cannot be adequately addressed by handling the problems regarding the exposing and developing devices and the problems regarding the photothermographic material separately, as has often been the case in the past.

[0007]

[Patent Document 1]

United States Patent (USP) No. 3152904

[Patent Document 2]

USP No. 3457075

[Patent Document 3]

USP No. 2910377
[Patent Document 4]
Japanese Patent Application Publication (JP-B) No. 43-4924
[Non-Patent Document 1]
"Thermally Processed Silver Systems," (Imaging Processes and Materials)
Neblette, 8th edition, edited by D. Klosterboer, compiled by J. Sturge, V. Walworth and A. Shepp, Chapter 9, page 279, 1989

[0008]

[Problems to be Solved by the Invention]

The present invention intends to solve the above problems in the prior art and has an object to develop a photosensitive material that is adapted for high speed processing and can form an output image even in a developing device with short image processing time.

[0009]

[Means for Solving the Problems]

The object of the present invention is achieved by the following photothermographic material:

(1) An image forming method using a photothermographic material comprising a photosensitive silver halide, a reducing agent, a binder and a non-photosensitive organic silver salt, wherein:

the photothermographic material is discharged from a thermal developing device within 35 seconds after heating for thermal development is ceased.

(2) The method of (1), wherein, when the photothermographic material is exposed with an amount of light sufficient to make image density of 1.0 by a thermal development of 14 seconds, thermal development for 16 seconds yields an image density of 1.0 to 1.3.

(3) The method of claim (1) or (2), wherein the non-photosensitive organic silver salt contains 30 mol% to 100 mol% of silver behenate.

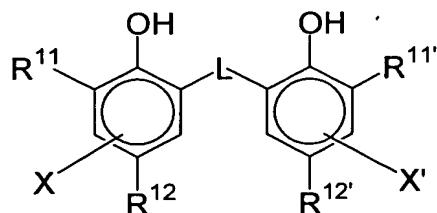
(4) The method of any one of (1) to (3), wherein the photothermographic material includes at least one type of development accelerator.

(5) The method of any one of (1) to (4), wherein the reducing agent is a bisphenol reducing agent.

(6) The method of (5), wherein the reducing agent is a compound represented by the following general formula (R):

General formula (R)

[Formula 2]



wherein R¹¹ and R^{11'} each independently represent one of a secondary and a tertiary alkyl group having 3 to 15 carbon atoms, R¹² and R^{12'} each independently represent a hydrogen atom or a substituent capable of substituting for a hydrogen atom on a benzene ring, L represents one of a -S- group and a -CHR¹³- group, R¹³ represents one of a hydrogen atom

and an alkyl group having 1 to 20 carbon atoms, and X^1 and $X^{1'}$ each independently represent a hydrogen atom or a substituent capable of substituting for a hydrogen atom on a benzene ring.

[0010]

- (7) The method of any one of (1) to (6), wherein the photothermographic material includes at least one type of phthalazine compound.
- (8) The method of (7), wherein the content of the phthalazine compound is 0.01 mol to 10 mol per one mol of applied silver.
- (9) The method of any one of (1) to (8), wherein the photothermographic material includes at least one type of mercapto compound.
- (10) The method of any one of (1) to (9), wherein the photothermographic material includes at least one type of benzotriazole compound.
- (11) The method of any one of (1) to (10), wherein the photothermographic material includes a thermal solvent having a melting point of 50 °C to 200 °C.

[0011]

The present invention will be described below in detail.

[0012]

[Embodiments]

In a developing system using a photothermographic material, a photosensitive material is exposed, conveyed to a heating section for thermal development, and discharged from a developing device. If, however, the photosensitive material is discharged immediately after the thermal development, the photosensitive material is exposed to light while being still hot, which is a main cause for a defective printout. Thus, the developing device generally includes a cooling zone for cooling the photosensitive material after thermal development. Processing speed per sheet of photosensitive material is improved by shortening the distance of the cooling zone or increasing conveyance speed in the cooling zone. In the image forming method using the photothermographic material of the invention, the photosensitive material, which is a photothermographic material, is discharged from the thermal developing device within 35 seconds after heating of the photosensitive material for thermal development is stopped. By shortening the cooling time in the cooling zone, the present inventor has succeeded in increasing the processing time per sheet of photosensitive material.

However, as described above, when the cooling time is too short, defective printouts are likely to be formed, and blurring may be formed in sequentially outputted images.

[0013]

The present inventor has studied diligently, and as a result, has found that, in order to obtain a stable output image, it is important that developing is finished during the heating time for thermal development.

Namely, when the cooling time is long as in the related art, a stable output image is obtained even if the development is not completely finished during heating but the development is finished before the photosensitive material is discharged from the developing device. However, when the cooling time is short, blurring may be formed in a discharged image if development is not completely finished during thermal development.

In order to completely finish development during heating for thermal development, it is important to produce a photothermographic material having high-speed

developing ability and giving a constant density by thermal development of short duration. However, simply increasing the high-speed developing ability also leads to increased fogging. Thus, developing a technique for increasing the high-speed developing ability without causing fogging is important.

The present inventor has found that a photothermographic material having the following composition is essential in order to achieve two conflicting phenomena, i.e., improving developing performance and preventing fogging, at the same time.

The photothermographic material according to the invention will be described below in detail.

[0014]

(Description of non-photosensitive organic silver salt)

1) Composition

The organic silver salt particle according to the invention is relatively stable to light but serves as to supply silver ions and forms silver images when heated to 80°C or higher in the presence of an exposed photosensitive silver halide and a reducing agent. The organic silver salt may be any organic material containing a source capable of reducing silver ions. Such non-photosensitive organic silver salt is disclosed, for example, in Japanese Patent Application Laid-Open (JP-A) Nos. 6-130543, 8-314078, 9-127643, 10-62899 (paragraph Nos. 0048 to 0049), 10-94074, and 10-94075, EP-A No. 0803764A1 (page 18, line 24 to page 19, line 37), EP-A Nos. 962812A1 and 1004930A2, JP-A Nos. 11-349591, 2000-7683, and 2000-72711, and the like. A silver salt of organic acid, particularly, a silver salt of long chained aliphatic carboxylic acid (having 10 to 30, preferably, 15 to 28 carbon atoms) is preferable. Preferred examples of the silver salt of the fatty acid can include, for example, silver lignocerate, silver behenate, silver arachidinic acid, silver stearate, silver oleate, silver laurate, silver capronate, silver myristate, silver palmitate, silver erucic acid and mixtures thereof.

In the invention, among the fatty acid silver salts, it is preferred to use a fatty acid silver salt with the silver behenate content of 30 mol% to 100 mol%, more preferably, 50 mol% to 100 mol%, further preferably, 85 mol% to 100 mol%, most preferably, 95 mol% to 100 mol%. Further, it is preferred to use a fatty acid silver salt with the silver erucic acid content of 2 mol% or less, more preferably, 1 mol% or less, further preferably, 0.1 mol% or less.

[0015]

It is preferred that the content of the silver stearate is 1 mol% or less. When the content of the the silver stearate is 1 mol% or less, a silver salt of organic acid having low Dmin, high photosensitivity and excellent image storability can be obtained. The content of the silver stearate above-mentioned, is preferably 0.5 mol% or less, more preferably, the silver stearate is not substantially contained.

[0016]

Further, in the case the silver salt of organic acid includes silver arachidinic acid, it is preferred that the content of the silver arachidinic acid is 6 mol% or less in order to obtain a silver salt of organic acid having low Dmin and excellent image storability. The content of the silver arachidinic acid is more preferably 3 mol% or less.

[0017]

2) Shape

There is no particular restriction on the shape of the organic silver salt usable in

the invention and it may be a needle-like, bar-like, plate-like or flaky shape.

In the invention, a flaky-shaped organic silver salt is preferred. A short needle-like, rectangular, cuboidal or potato-like indefinite-shaped particle with the major axis to minor axis ratio being 5 or less is also used preferably. Such organic silver particle has a feature of less fogging during thermal development compared with long needle-like particles with the major axis to minor axis length ratio of 5 or more. Particularly, a particle with the major axis to minor axis ratio of 3 or less is preferred since it can improve the mechanical stability of the coating film. In the present specification, the flaky shaped organic silver salt is defined as follows. When an organic acid silver salt is observed under an electron microscope, calculation is made while approximating the shape of an organic acid silver salt particle to a rectangular body and assuming each side of the rectangular body as a , b , c from the shorter side (c may be identical with b) and determining x based on numerical values a , b for the shorter side as below.

$$x = b/a$$

[0018]

x is determined as described above for each of about 200 particles and those capable of satisfying the relation: x (average) ≥ 1.5 as an average value x is defined as a flaky shape. The relation is preferably $30 \geq x$ (average) ≥ 1.5 and, more preferably, $15 \geq x$ (average) ≥ 1.5 . The needle-like shape is expressed as $1 \leq x$ (average) < 1.5 .

[0019]

In the flaky shaped particle, a can be regarded as a thickness of a plate particle having a principal plane with b and c being as the sides. a in average is preferably 0.01 μm to 0.3 μm and, more preferably, 0.1 μm to 0.23 μm . c/b in average is preferably 1 to 9, more preferably, 1 to 6 and, further preferably, 1 to 4 and, most preferably, 1 to 3.

[0020]

By controlling the sphere equivalent diameter to 0.05 μm to 1 μm , it causes less agglomeration in the photosensitive material and image storability is improved. The spherical equivalent diameter is preferably 0.1 μm to 1 μm . In the invention, the sphere equivalent diameter can be measured by a method of photographing a sample directly by using an electron microscope and then image-processing negative images.

In the flaky-shaped particle, the sphere equivalent diameter of the particle/ a is defined as an aspect ratio. The aspect ratio of the flaky particle is, preferably, 1.1 to 30 and, more preferably, 1.1 to 15 from the viewpoint of causing less agglomeration in the photosensitive material and improving the image storability.

[0021]

As the particle size distribution of the organic silver salt, mono-dispersion is preferred. In the mono-dispersion, the percentage for the value obtained by dividing the standard deviation for the length of minor axis and major axis by the minor axis and the major axis respectively is, preferably, 100% or less, more preferably, 80% or less and, further preferably, 50% or less. The shape of the organic silver salt can be measured by determining dispersion of an organic silver salt as transmission type electron microscopic images. Another method of measuring the mono-dispersion is a method of determining of the standard deviation of the volume weighted mean diameter of the organic silver salt in which the percentage for the value divided by the volume weight mean diameter (variation coefficient), is preferably, 100% or less, more preferably, 80% or less and,

further preferably, 50% or less. The mono-dispersion can be determined from the particle size (volume weighted mean diameter) obtained, for example, by a measuring method of irradiating a laser beam to an organic silver salt dispersed in a liquid, and determining an auto-correlation function of the fluctuation of scattered light to the change of time.

[0022]

3) Preparation

Known methods can be used as the methods for producing and dispersing organic acid salt used in the invention. For example, reference can be made to JP-A No. 10-62899, EP-A Nos. 0803763A1 and 0962812A1, JP-A Nos. 11-349591, 2000-7683, 2000-72711, 2001-163889, 2001-163890, 2001-163827, 2001-33907, 2001-188313, 2001-83652, 2002-6442, 2002-49117, 2002-31870 and 2002-107868.

[0023]

When a photosensitive silver salt is present during dispersion of the organic silver salt, fog increases and the sensitivity becomes remarkably lower, so it is more preferred that the photosensitive silver salt is not substantially contained during dispersion. In the invention, the amount of the photosensitive silver salt to be dispersed in the aqueous dispersion is preferably 1 mol% or less, more preferably, 0.1 mol% or less per one mol of the organic acid silver salt in the solution and, further preferably, positive addition of the photosensitive silver salt is not conducted.

[0024]

In the invention, the photosensitive material can be prepared by mixing an aqueous dispersion of an organic silver salt and an aqueous dispersion of a photosensitive silver salt and the mixing ratio between the organic silver salt and the photosensitive silver salt can be selected depending on the purpose. The ratio of the photosensitive silver salt to the organic silver salt is, preferably, within a range from 1 mol% to 30 mol%, more preferably, within a range from 2 mol% to 20 mol% and, particularly preferably, 3 mol% to 15 mol%. A method of mixing two or more kinds of aqueous dispersions of organic silver salts and two or more kinds of aqueous dispersions of photosensitive silver salts upon mixing is used preferably for controlling the photographic properties.

[0025]

4) Added amount

Although the organic silver salt of the invention can be used in any desired amount, the total amount of silver coating including silver halide is preferably 0.1 to 5.0 g/m², more preferably 0.3 to 3.0 g/m², and particularly preferably 0.5 to 2.0 g/m². The total amount of silver coating is preferably 1.8 g/m² or less, and more preferably 1.6 g/m² in order to improve image storability. If a preferable reducing agent of the invention is used, a sufficient image density can be obtained even with such a low silver amount.

[0026]

(Thermal solvent)

The photothermographic material in the invention preferably contains a thermal solvent. The thermal solvent is defined as a material capable of lowering the thermal development temperature by 1°C or more with regard to the thermal solvent-containing photothermographic material, compared with the photothermographic material not containing the thermal solvent. Further preferably, this is the material capable of lowering the thermal development temperature by 2°C or more and, particularly, capable of

lowering the temperature by 3°C or more. For the photothermographic material A containing the thermal solvent and the photothermographic material B not containing the thermal solvent, relative to the photothermographic material A, the material is defined as a thermal solvent when the thermal development temperature is 119°C or lower for obtaining the density to be obtained by exposing the photothermographic material B and processing the same at a thermal development temperature of 120°C for a thermal development time of 20 seconds, by the photothermographic material A with the identical amount of exposure and thermal development time.

[0027]

The thermal solvent of the invention has polar groups as substituent groups, and, though not limiting, those expressed by formula (1) are preferred.

[0028]

Formula (1)

$(Y)_nZ$

[0029]

In formula (1), Y represents an alkyl group, an alkenyl group, an alkynyl group, an aryl group, or a heterocyclic group; Z represents a group selected from a hydroxyl group, a carboxyl group, an amino group, an amido group, a sulfoamido group, a phosphoamido group, a cyano group, an imido, an ureido, a sulfoxide, a sulfone, a phosphine, a phosphineoxide, or an nitrogen-containing heterocyclic group; n represents an integer from 1 to 3, which is 1 in the case Z is a monovalent group, and is the same as the valence of Z in the case Z is a divalent group or a group with higher valence. In the case n is a numeral 2 or higher, plural Y's may be the same or different.

Y may further contain a substituent group, and may have a group expressed by Z as the substituent group.

[0030]

Y is explained in further detail below. In formula (1), Y may be a straight chain, a branched, or a cyclic alkyl group (preferably having 1 to 40 carbons, more preferably 1 to 30 carbons, and most preferably, 1 to 25 carbons; more specifically, there can be mentioned a methyl, an ethyl, an n-propyl, an iso-propyl, a sec-butyl, a t-butyl, a t-octyl, an n-amyl, a t-amyl, an n-dodecyl, an n-tridecyl, an octadecyl, an icosyl, a docosyl, a cyclopentyl, a cyclohexyl, and the like), an alkenyl group (preferably having 2 to 40 carbons, more preferably 2 to 30 carbons, and most preferably, 2 to 25 carbons; more specifically, there can be mentioned a vinyl, an allyl, a 2-butenyl, a 3-pentenyl, and the like), an aryl group (preferably having 6 to 40 carbons, more preferably 6 to 30 carbons, and most preferably, 6 to 25 carbons; more specifically, there can be mentioned a phenyl, a p-methylphenyl, a naphthyl, and the like), and a heterocyclic group (preferably having 2 to 20 carbons, more preferably 2 to 16 carbons, and most preferably, 2 to 12 carbons; more specifically, there can be mentioned a pyridyl, a pyradyl, an imidazoyl, a pyrrolisyl, and the like). These substituents may be further substituted by other substituents. Furthermore, these substituents may be combined with each other to form a ring.

[0031]

Y may further contain substituents, and as examples of the substituents, there can be mentioned a halogen atom (a fluorine atom, a chlorine atom, a bromine atom, or an iodine atom), an alkyl group (a straight chain, a branched, or a cyclic alkyl group, inclusive

of bicycloalkyl group and an active methine group), an alkenyl group, an alkynyl group, an aryl group, or a heterocyclic group (irrespective of the position of substitution), an acyl group, an alcoxylcarbonyl group, an aryloxycarbonyl group, a heterocyclic oxycarbonyl group, a carbamoyl group, an N-acylcarbamoyl group, an N-sulfonylcarbamoyl group, an N-carbamoylcarbamoyl group, a thiocarbamoyl group, an N-sulfamoylcarbamoyl group, a carbazoyl group, a carboxy group or a salt thereof, an oxaryl group, an oxamoyl group, a cyano group, a carbonimidoyl group, a formyl group, a hydroxyl group, an alkoxy group (inclusive of a group containing a repetition of ethyleneoxy group or propyleneoxy group), an aryloxy group, a heterocyclic oxy group, an acyloxy group, (an alkoxy or aryloxy) carbonyloxy group, a carbamoyloxy group, a sulfonyloxy group, an amino group, (an alkyl, an aryl, or a heterocyclic) amino group, an acylamino group, a sulfonamido group, an ureido group, a thioureido group, an imido group, (an alkoxyl or an aryloxy) carbonylamino group, a sulfamoylamino group, a semicarbazido group, a thiosemicarbazido group, an ammonio group, an oxamoylamino group, an N-(alkyl or aryl) sulfonylureido group, an N-acylureido group, an N-acylsulfamoyl group, a nitro group, a heterocyclic group containing a tertialized nitrogen atom (for instance, a pyridinio group; an imidazolio group, a quinolinio group, an isoquinolinio group), an isocyano group, an imino group, a mercapto group, (an alkyl, an aryl, or a heterocyclic) thio group, (an alkyl, an aryl, or a heterocyclic) dithio group, (an alkyl or an aryl) sulfonyl group, (an alkyl or an aryl) sulfinyl group, a sulfo group or a salt thereof, a sulfamoyl group, an N-acylsulfamoyl group, an N-sulfonylsulfamoyl group or a salt thereof, a phosphino group, a phosphinyl group, a phosphinyloxy group, a phosphinylamino group, a silyl group, and the like. An active methine group herein signifies a methine group substituted by two electron-attracting groups, and an electron-attracting group means an acyl group, an alcoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group, a sulfamoyl group, a trifluoromethyl group, a cyano group, a nitro group, or a carbonimidoyl group. The two electron-attracting groups may combine with each other to form a ring structure. A salt as referred herein signifies a cation such as that of an alkali metal, an alkaline earth metal, a heavy metal, and the like, or an organic cation such as an ammonium ion, phosphonium ion, and the like. These substituents may further be substituted by the substituents enumerated above. Y may further contain a group expressed by Z as a substituent.

[0032]

As the reason why the thermal solvent shows the effect of the invention, it is believed that the thermal solvent melts at a temperature in the vicinity of the development temperature to show compatibility with the substance related with the development, and that it enables reaction at a temperature lower than the case no thermal solvent is added to the system. Thermal development is a reduction reaction in which carboxylic acids and silver ion carriers having relatively high polarity contribute to the reaction. Thus, it is preferred to incorporate a thermal solvent having polar groups to form a reaction field having an appropriate degree of polarity.

The melting point of the thermal solvent of the invention is in a range not lower than 50°C but not higher than 200°C, but is preferably in a range not lower than 60°C but not higher than 150°C. In the case of a photothermographic material in which stability with respect to external environment such as image storability and the like is stressed, in particular, thermal solvent having a melting point in a range not lower than 100°C but not higher than 150°C is preferred.

[0033]

Specific examples of thermal solvents of the invention are given below, but it should be understood that the invention is not limited thereto. Melting point of the solvent is given in parenthesis.

N-methyl-N-nitroso-p-toluenesulfonamide (61°C), 1,8-octanediol (62°C), phenyl benzoate (67°C - 71°C), hydroquinone diethyl ether (67°C - 73°C), ε-caprolactam (68°C - 70°C), diphenyl phosphate (68°C - 70°C), (±)-2-hydroxyoctanoic acid (68°C - 71°C), (±)-3-hydroxydodecanoic acid (68°C - 71°C), 5-chloro-2-methylbenzothiazole (68°C - 71°C), β-naphthyl acetate (68°C - 71°C), butyl alcohol (68°C - 73°C), (±)-2-hydroxydecanoic acid (69°C - 72°C), 2,2,2-trifluoroacetamide (69 - 72°C), pyrazole (69°C), (±)-2-hydroxyundecanoic acid (70°C - 73°C), N,N-diphenyl formamide (71°C - 72°C), dibenzyl disulfide (71°C - 72°C), (±)-3-hydroxyundecanoic acid (71°C - 74°C), 2,2'-dihydroxy-4-methoxybenzophenone (71°C), 2,4-dinitrotoluene (71°C), 2,4-dimethoxybenzaldehyde (71°C), 2,6-di-t-butyl-4-methylphenol (71°C), 2,6-dichlorobenzaldehyde (71°C), diphenylsulfoxide (71°C), stearic acid (71°C), 2,5-dimethoxynitrobenzene (72°C - 73°C), 1,10-decanediol (72°C - 74°C), (R)-(-)-3-hydroxytetradecanoic acid (72°C - 75°C), 2-tetradecylhexadecanoic acid (72°C - 75°C),

[0034]

2-methoxynaphthalene (72°C - 75°C), methyl 3-hydroxy-2-naphthoate (72°C - 76°C), tristearin (73.5°C), dotriacontane (74°C - 75°C), flavanone (74°C - 78°C), 2,5-diphenyloxazole (74°C), 8-quinolinol (74°C), o-chlorobenzyl alcohol (74°C), oleic acid amide (75°C - 76°C), (±)-2-hydroxydodecanoic acid (75°C - 78°C), n-hexatriacontane (75°C - 79°C), iminodiacetonitrile (75°C - 79°C), p-chlorobenzyl alcohol (75°C), diphenyl diphthalate (75°C), N-methylbenzamide (76°C - 78°C), (±)-2-hydroxytridecanoic acid (76°C - 79°C), 1,3-diphenyl-1,3-propanedione (76°C - 79°C), N-methyl-p-toluenesulfonamide (76°C - 79°C), 3'-nitroacetophenone (76°C - 80°C), 4-phenylcyclohexanone (76 °C – 80°C), eicosanic acid (76°C), 4-chlorobenzophenone (77°C - 78°C), (±)-3-hydroxytetradecanoic acid (77°C - 80°C), 2-hexadecyloctadecanoic acid (77°C - 80°C), p-nitrophenyl acetate (77°C - 80°C), 4'-nitroacetophenone (77°C - 81°C), 12-hydroxystearic acid (77°C), α,α'-dibromo-m-xylene (77°C), 9-methylanthracene (78°C - 81°C), 1,4-cyclohexanedione (78°C), m-diethylaminophenol (78°C), methyl m-nitrobenzoate (78°C), (±)-2-hydroxytetradecanoic acid (79°C - 82°C), l-(phenylsulfonyl)indole (79°C), di-p-tolylmethane (79°C), propioneamide (79°C), (±)-3-hydroxytridecanoic acid (80 °C - 83°C), guaiacol glycerin ether (80°C - 85°C), octanoyl-N-methylglucamide (80°C - 90°C), o-fluoroacetanilide (80°C), acetanilide (80°C),

[0035]

docosanoic acid (81°C - 82°C), p-bromobenzophenone (81°C), triphenylphosphine (81 °C), dibenzofuran (82.8°C), (±)-2-hydroxypentadecanoic acid (82°C - 85°C), 2-octadecyleicosanic acid (82°C - 85°C), 1,12-dodecanediol (82°C), methyl 3,4,5-trimethoxybenzoate (83°C), p-chloronitrobenzene (83°C), (±)-3-hydroxyhexadecanoic acid (84 - 85°C), o-hydroxybenzyl alcohol (84 °C - 86°C), l-triacontanol (84°C - 88°C), o-aminobenzyl alcohol (84°C), 4-methoxybenzyl acetate (84°C), (±)-2-hydroxyhexadecanoic acid (85°C - 88°C), m-dimethylaminophenol (85°C), p-dibromobenzene (86°C - 87°C), methyl 2,5-dihydroxybenzoate (86 - 88°C), (±)-3-hydroxypentadecanoic acid (86 - 89°C), 4-benzylbiphenyl (86°C), p-fluorophenylacetic acid (86°C), 1,14-tetradecanediol (87°C - 89°C), 2,5-dimethyl-2,5-hexanediol (87°C - 90°C), p-pentylbenzoic acid (87°C - 91°C), α-(trichloromethyl)benzyl acetate (88°C - 89°C), 4,4'-dimethylbenzoin (88°C), diphenyl

carbonate (88°C), m-dinitrobenzene (89.57°C), (3R,5R)-(+)-2,6-dimethyl-3,5-heptanediol (90°C - 93°C), (3S,5S)-(-)-2,6-dimethyl-3,5-heptanediol (90°C - 93°C), cyclohexanoneoxime (90°C), p-bromoiodobenzene (91°C - 92°C), 4,4'-dimethylbenzophenone (92°C - 95°C), triphenylmethane (92°C - 95°C), stearic acid anilide (92°C - 96°C), p-hydroxyphenyl ethanol (92°C), monoethylurea (92°C), acenaphthylene (93.5°C – 94.5°C), m-hydroxyacetophenone (93°C - 97°C), xylitol (93°C - 97°C), p-iodophenol (93°C), methyl p-nitrobenzoate (94°C - 98°C),

[0036]

p-nitrobenzyl alcohol (94°C), 1,2,4-triacetoxybenzene (95°C - 100°C), 3-acetylbenzonitrile (95°C - 103°C), ethyl 2-cyano-3,3-diphenylacrylate (95°C - 97°C), 16-hydroxyhexadecanoic acid (95°C - 99°C), D(-)-ribose (95°C), o-benzoylbenzoic acid (95°C), α,α' -dibromo-o-xylene (95°C), benzyl (95°C), iodoacetamide (95°C), n-propyl p-hydroxylbenzoate (96°C - 97°C), flavone (96°C - 97°C), 2-deoxy-D-ribose (96°C - 98°C), lauryl gallate (96°C - 99°C), 1-naphthol (96°C), 2,7-dimethylnaphthalene (96°C), 2-chlorophenylacetic acid (96°C), acenaphthene (96°C), dibenzyl terephthalate (96°C), fumaronitrile (96°C), 4'-amino-2',5'-diethoxybenzanilide (97°C - 100°C), phenoxyacetic acid (97°C - 100°C), 2,5-dimethyl-3-hexyne-2,5-diol (97°C), D-sorbitol (97°C), m-aminobenzyl alcohol (97°C), diethyl acetamidomalonate (97°C), 1,10-phenanthroline monohydrate (98°C - 100°C), 2-hydroxy-4-methoxy-4'-methylbenzophenone (98 - 100°C), 2-bromo-4'-chloroacetophenone (98°C), methylurea (98°C), 4-phenoxyphthalonitrile (99°C - 100°C), o-methoxybenzoic acid (99°C - 100°C), p-butylbenzoic acid (99°C - 100°C), xanthene (99°C - 100°C), pentafluorobenzoic acid (99°C - 101°C), phenanthrene (99°C), p-t-butylphenol (100.4°C), 9-fluorenylmethanol (100°C - 101°C), 1,3-dimethylurea (100°C - 102°C), 4-acetoxyindole (100°C - 102°C), 1,3-cyclohexanedione (100°C), stearic acid amide (100°C), tri-m-tolylphosphine (100°C), 4-biphenylmethanol (101 - 102°C), 1,4-cyclohexanediol (mixture of cis- and trans-)(101°C), α,α' -dichloro-p-xylene (101°C), 2-t-butylanthraquinone (102°C), dimethylfumaric acid (102°C), 3,3-dimethylglutaric acid (103°C - 104°C), 2-hydroxy-3-methyl-2-cyclopenten-1-one (103°C), 4-chloro-3-nitroaniline (103°C), N,N-diphenylacetamide (103°C), 3(2)-t-butyl-4-hydroxyanisole (104°C - 105°C), 4,4'-dimethylbenzyl (104°C - 105°C), 2,2-bis(hydroxymethyl)-2,2',2''-nitrilotriethanol (104°C), m-trifluoromethylbenzoic acid (104°C), 3-pentanol (105°C - 108°C), 2-methyl-1,4-naphthoquinone (105°C), $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-m-xylene (105°C), 4-chlorophenylacetic acid (106°C), 4,4'-difluorobenzophenone (107.5 °C – 108.5°C),

[0037]

2,4-dichloro-1-naphthol (107°C – 108°C), L-ascorbic acid palmitic acid ester (107 °C – 117°C), 2,4-dimethoxybenzoic acid (108°C – 109°C), o-trifluoromethylbenzoic acid (108 °C – 109°C), p-hydroxyacetophenone (109°C), dimethylsulfone (109°C), 2,6-dimethylnaphthalene (110 °C – 111°C), 2,3,5,6-tetramethyl-1,4-benzoquinone (110°C), tridecane diacid (110°C), triphenylchloromethane (110 °C), fluoranthene (110°C), laurylamide (110°C), 1,4-benzoquinone (111°C), 3-benzylindole (111°C), resorcinol (111°C), 1-bromomethane (112.3°C), 2,2-bis(bromomethyl)-1,3-propanediol (112 – 114°C), p-ethylbenzoic acid (113.5°C), 1,4-diacetoxy-2-methylnaphthalene (113°C), 1-ethyl-2,3-piperadinedione (113°C), 4-methyl-2-nitroaniline (113°C), L-ascorbic acid dipalmitic acid ester (113°C),

[0038]

o-phenoxybenzoic acid (113 °C), p-nitrophenol (113°C), methyl(diphenyl)phosphine oxide (113°C), cholesterol acetate (114°C – 115°C), 2,6-dimethylbenzoic acid (114 °C – 116°C), 3-nitrobenzonitrile (114°C), m-nitroaniline (114°C), ethyl α-D-glucoside (114°C), acetanilide (115°C – 116°C), (±)-2-phenoxypropionic acid (115°C), 4-chloro-1-naphthol (116°C – 117°C), p-nitrophenylacetonitrile (116°C – 117°C), ethyl p-hydroxybenzoate (116°C), p-isopropylbenzoic acid (117°C – 118°C), D(+)-galactose (118°C – 120°C), o-dinitrobenzene (118°C), benzyl p-benzyloxybenzoate (118°C), 1,3,5-tribromobenzene (119°C), 2,3-dimethoxybenzoic acid (120°C - 122°C), 4-chloro-2-methylphenoxyacetic acid (120°C), meso-erythritol (121.5°C), 9,10-dimethyl-1,2-benzanthracene (122°C – 123°C), 2-naphthol (122°C), N-phenylglycine (122°C), bis(4-hydroxy-3-methylphenyl)sulfide (122°C), p-hydroxybenzyl alcohol (124.5 °C – 125.5°C), 2',4'-dihydroxy-3'-propylacetophenone (124°C – 127°C), 1,1-bis(4-hydroxyphenyl)ethane (124°C), m-fluorobenzoic acid (124°C), diphenylsulfone (124°C), 2,2-dimethyl-3-hydroxypropionic acid (125°C), 3,4,5-trimethoxycinnamic acid (125°C), o-fluorobenzoic acid (126.5°C), isonitrosoacetophenone (126 – 128°C), 5-methyl-1,3-cyclohexanedione (126°C), 4-benzoylbutyric acid (127°C), methyl p-hydroxybenzoate (127°C),

[0039]

p-bromonitrobenzene (127°C), 3,4-dihydrocyphenylacetic acid (128°C – 130°C), 5α-cholestane-3-one (128°C – 130°C), 6-bromo-2-naphthol (128°C), isobutylamide (128°C), 1-naphthylacetic acid (129°C), 2,2-dimethyl-1,3-propanediol (129°C), p-diiodobenzene (129°C), dodecane diacid (129°C), 4,4'-dimethoxybenzyl (131°C – 133°C), dimethylolurea (132.5°C), o-ethoxybenzamide (132°C – 134°C), cebacic acid (132°C), p-toluenesulfonamide (134°C), salicylanilide (135°C), β-cyosterol (136 – 137°C), 1,2,4,5-tetrachlorobenzene (136°C), 1,3-bis(1-hydroxy-1-methylethyl)benzene (137°C), phthalonitrile (138°C), 4-n-propylbenzoic acid (139°C), 2,4-dichlorophenoxyacetic acid (140.5°C), 2-naphthylacetic acid (140°C), methyl terephthalate (140°C), 2,2-dimethylsuccinic acid (141°C), 2,6-dichlorobenzonitrile (142.5°C – 143.5°C), o-chlorobenzoic acid (142°C), 1,2-bis(diphenylphosphino)ethane (143°C – 144°C), α,α,α-tribromomethylphenylsulfone (143°C), D(+)-xylose (144°C – 145°C), phenylurea (146°C), n-propyl gallate (146°C), 4,4'-dichlorobenzophenone (147°C - 148°C), 2',4'-dihydroxyacetophenone (147°C), cholesterol (148.5°C), 2-methyl-1-pentanol (148°C), 4,4'-dichlorodiphenylsulfone (148°C), diglycolic acid (148°C), adipic acid (149°C - 150°C), 2-deoxy-D-glucose (149°C), diphenylacetic acid (149°C), and o-bromobenzoic acid (150°C).

[0040]

In the invention, the thermal solvent is preferably added in a range of from 0.01 g/m² to 5.0 g/m², more preferably from 0.05 g/m² to 2.5 g/m², and most preferably, from 0.1 g/m² to 1.5 g/m². Preferably, the thermal solvent is incorporated in the image forming layer.

The thermal solvent may be used alone, but two or more types thereof may be added in combination.

[0041]

In the invention, the thermal solvent may be incorporated into photosensitive

material by being added into the coating solution, such as in the form of a solution, an emulsion dispersion, a solid particle dispersion, and the like.

As a well-known emulsion dispersion method, there can be mentioned a method comprising dissolving the thermal solvent in an auxiliary solvent such as oil, for instance, dibutyl phthalate, tricresyl phosphate, glyceryl triacetate, diethyl phthalate, and the like, as well as ethyl acetate, cyclohexanone, and the like; from which an emulsion dispersion is mechanically produced.

[0042]

As a solid particle dispersion method, there can be mentioned a method comprising dispersing the powder of the thermal solvent in a proper medium such as water, by means of ball mill, colloid mill, vibrating ball mill, sand mill, jet mill, roller mill, or ultrasonics, thereby obtaining a solid dispersion. In this case, there can also be used a protective colloid (such as polyvinyl alcohol), or a surface active agent (for instance, an anionic surface active agent such as sodium triisopropylnaphthalenesulfonate (a mixture of compounds having the isopropyl groups in different substitution sites)). In the mills enumerated above, generally used as the dispersion media are beads made of zirconia and the like, and Zr and the like eluting from the beads may be incorporated in the dispersion. Although depending on the dispersing conditions, the amount of Zr and the like generally incorporated in the dispersion is in a range of from 1 ppm to 1000 ppm. It is practically acceptable so long as Zr is incorporated in an amount of 0.5 mg or less with respect to 1 g of silver.

Preferably, a preservative (for instance, sodium benzoisothiazolinone salt) is added in the water dispersion. In the invention, furthermore, the thermal solvent is preferably used as a solid dispersion.

[0043]

(Description of reducing agent)

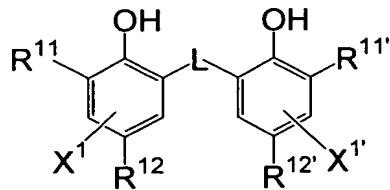
The photothermographic material of the invention preferably contains a reducing agent for the organic silver salt. The reducing agent for the organic silver salt may be any substance (preferably, organic substance) capable of reducing silver ions into metallic silver. Examples of the reducing agent are described in JP-A No. 11-65021 (paragraph Nos. 0043 to 0045) and EP-A 0803764A1 (p.7, line 34 to p. 18, line 12).

In the invention, a so-called hindered phenolic reducing agent or a bisphenol agent having a substituent at the ortho-position to the phenolic hydroxyl group is preferred, and the compound represented by the following general formula (R) is more preferred.

[0044]

General formula (R)

[Formula 3]



[0045]

(In the general formula (R), R¹¹ and R^{11'} each independently represent an alkyl

group having 1 to 20 carbon atoms. R^{12} and $R^{12'}$ each independently represents a hydrogen atom or a group capable of substituting for a hydrogen atom on a benzene ring. L represents a -S- group or a -CHR¹³- group. R¹³ represents a hydrogen atom or an alkyl group having 1 to 20 carbon atoms. X and X¹ each independently represents a hydrogen atom or a group capable of substituting for a hydrogen atom on a benzene ring.)

[0046]

Each of the substituents is to be described specifically.

1) R^{11} and $R^{11'}$

R^{11} and $R^{11'}$ each independently represents a substituted or unsubstituted alkyl group having 1 to 20 carbon atoms. The substituent for the alkyl group has no particular restriction, and examples thereof can include, preferably, aryl group, hydroxy group, alkoxy group, aryloxy group, alkylthio group, arylthio group, acylamino group, sulfoneamide group, sulfonyl group, phosphoryl group, acyl group, carbamoyl group, ester group, ureido group and a halogen atom.

[0047]

2) R^{12} and $R^{12'}$, X and X¹

R^{12} and $R^{12'}$ each independently represent a hydrogen atom or a group capable of substituting for a hydrogen atom on a benzene ring. X and X¹ also each independently represent a hydrogen atom or a group capable of substituting for a hydrogen atom on a benzene ring. Examples of the groups capable of substituting for a hydrogen atom on the benzene ring can include, preferably, alkyl group, aryl group, halogen atom, alkoxy group, and acylamino group.

[0048]

3) L

L represents a -S- group or a -CHR¹³- group. R¹³ represents a hydrogen atom or an alkyl group having 1 to 20 carbon atoms in which the alkyl group may have a substituent. Specific examples of the non-substituted alkyl group for R¹³ can include, for example, methyl group, ethyl group, propyl group, butyl group, heptyl group, undecyl group, isopropyl group, 1-ethylpentyl group, and 2,4,4-trimethylpentyl group. Examples of the substituent for the alkyl group can include, like substituent R¹¹, a halogen atom, an alkoxy group, alkylthio group, aryloxy group, arylthio group, acylamino group, sulfoneamide group, sulfonyl group, phosphoryl group, oxycarbonyl group, carbamoyl group, and sulfamoyl group.

[0049]

4) Preferred substituents

R^{11} and $R^{11'}$ are, preferably, a secondary or tertiary alkyl group having 3 to 15 carbon atoms, and specific examples thereof include isopropyl group, isobutyl group, t-butyl group, t-amyl group, t-octyl group, cyclohexyl group, cyclopentyl group, 1-methylcyclohexyl group, and 1-methylcyclopropyl group. R^{11} and $R^{11'}$ each represent, more preferably, tertiary alkyl group having 4 to 12 carbon atoms and, among them, t-butyl group, t-amyl group, 1-methylcyclohexyl group are further preferred, and t-butyl group is most preferred.

[0050]

R^{12} and $R^{12'}$ are, preferably, alkyl groups having 1 to 20 carbon atoms, and specific examples thereof include methyl group, ethyl group, propyl group, butyl group, isopropyl

group, t-butyl group, t-amyl group, cyclohexyl group, 1-methylcyclohexyl group, benzyl group, methoxymethyl group and methoxyethyl group. More preferred are methyl group, ethyl group, propyl group, isopropyl group, and t-butyl group. X and X¹ are, preferably, a hydrogen atom, halogen atom, or alkyl group, and more preferably, hydrogen atom.

[0051]

L is preferably a group -CHR¹³-.

R¹³ is, preferably, a hydrogen atom or an alkyl group having 1 to 15 carbon atoms. The alkyl group is preferably methyl group, ethyl group, propyl group, isopropyl group and 2,4,4-trimethylpentyl group. Particularly preferred R¹³ is a hydrogen atom, methyl group, propyl group or isopropyl group.

[0052]

In a case where R¹³ is a hydrogen atom, R¹² and R^{12'} each represents, preferably, an alkyl group having 2 to 5 carbon atoms, ethyl group and propyl group being more preferred and ethyl group being most preferred.

In a case where R¹³ is a primary or secondary alkyl group having 1 to 8 carbon atom, R¹² and R^{12'} each represents preferably methyl group. As the primary or secondary alkyl group of 1 to 8 carbon atoms for R¹³, methyl group, ethyl group, propyl group and isopropyl group are more preferred, and methyl group, ethyl group, and propyl group are further preferred.

In a case where each of R¹¹, R^{11'} and R¹², R^{12'} is methyl group, R¹³ is preferably a secondary alkyl group. In this case, the secondary alkyl group for R¹³ is preferably isopropyl group, isobutyl group and 1-ethylpentyl group, with isopropyl group being more preferred.

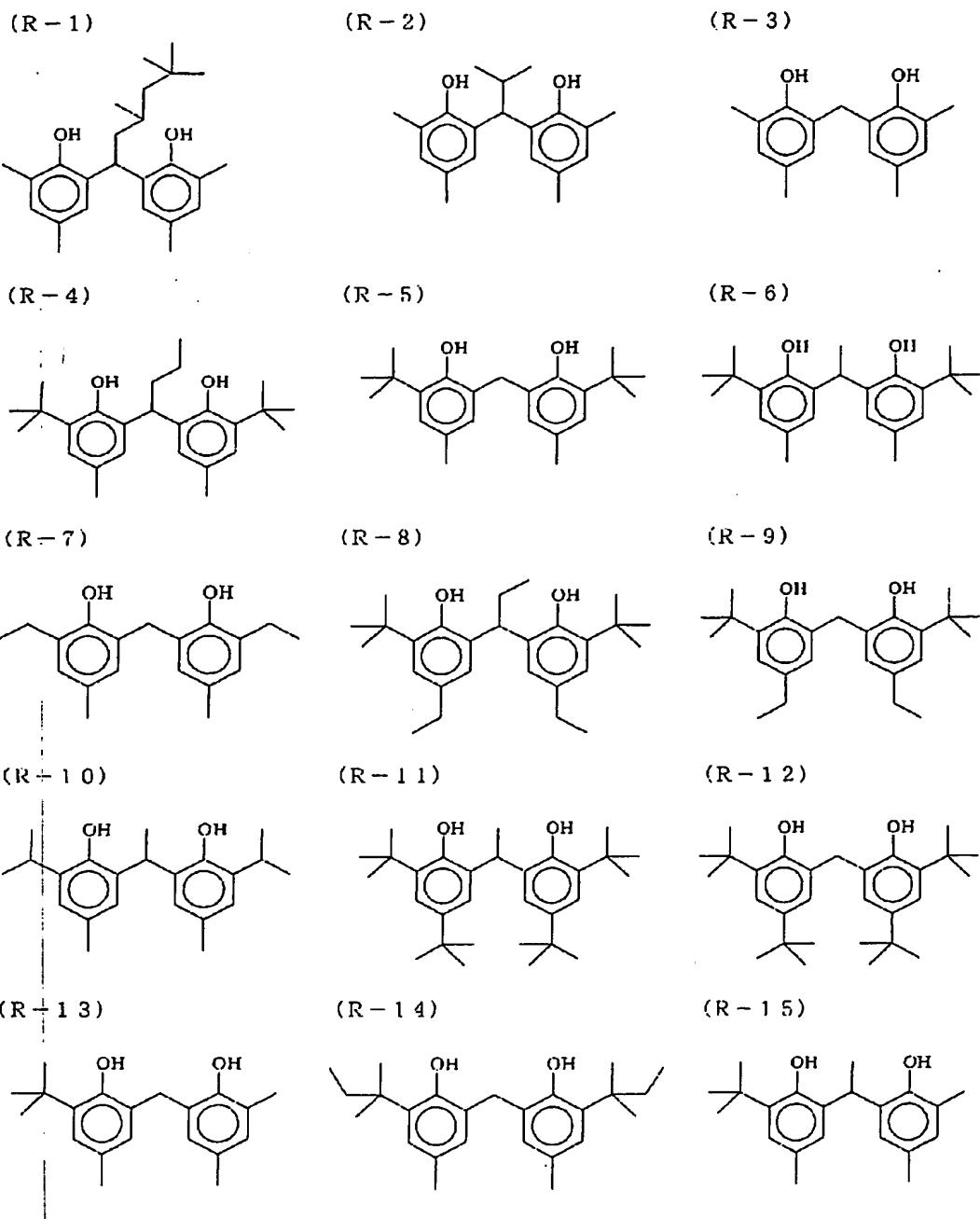
The reducing agent described above show various different thermo-developing performance depending on the combination of R¹¹, R^{11'} and R¹², R^{12'}, as well as R¹³. Since the thermo-developing performances can be controlled by using two or more kinds of reducing agents at various mixing ratios, it is preferred to use two or more kinds of reducing agents in combination depending on the purpose.

[0053]

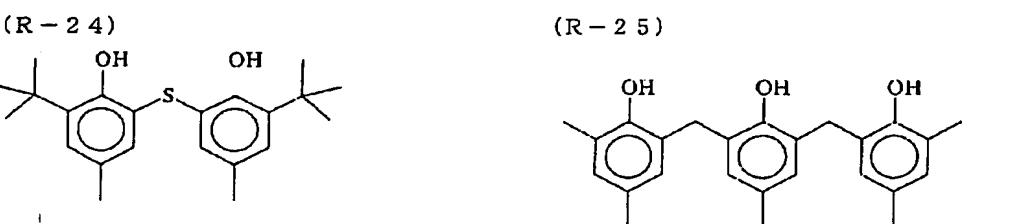
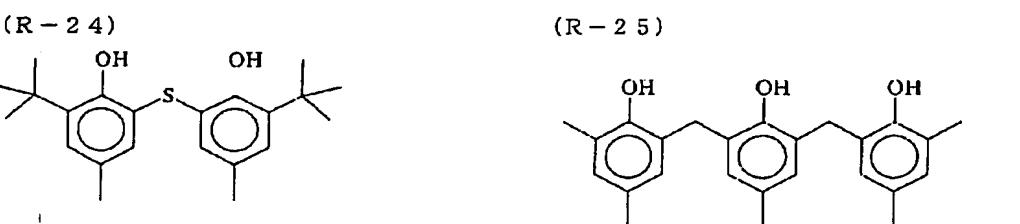
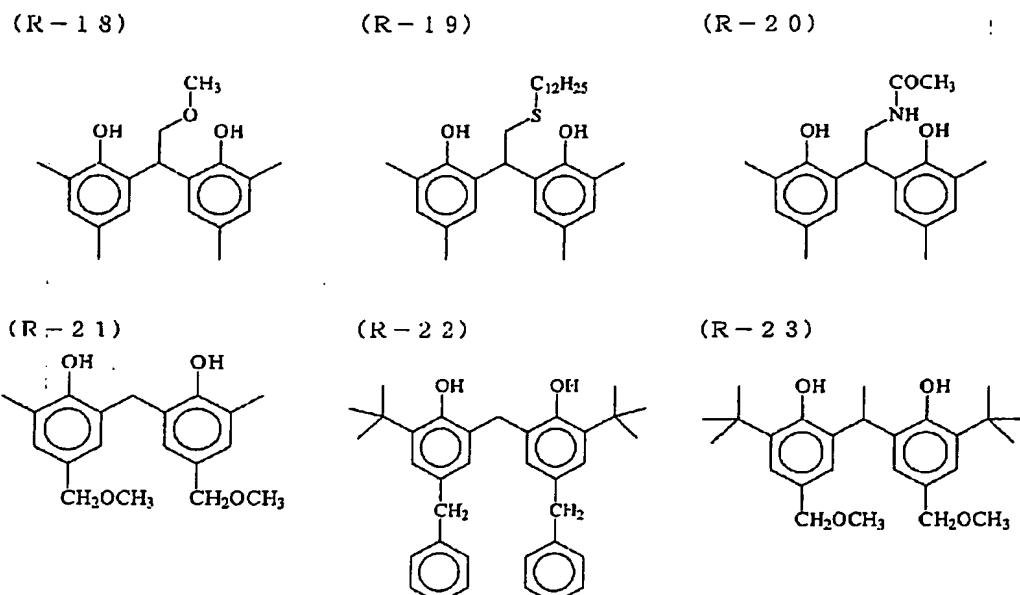
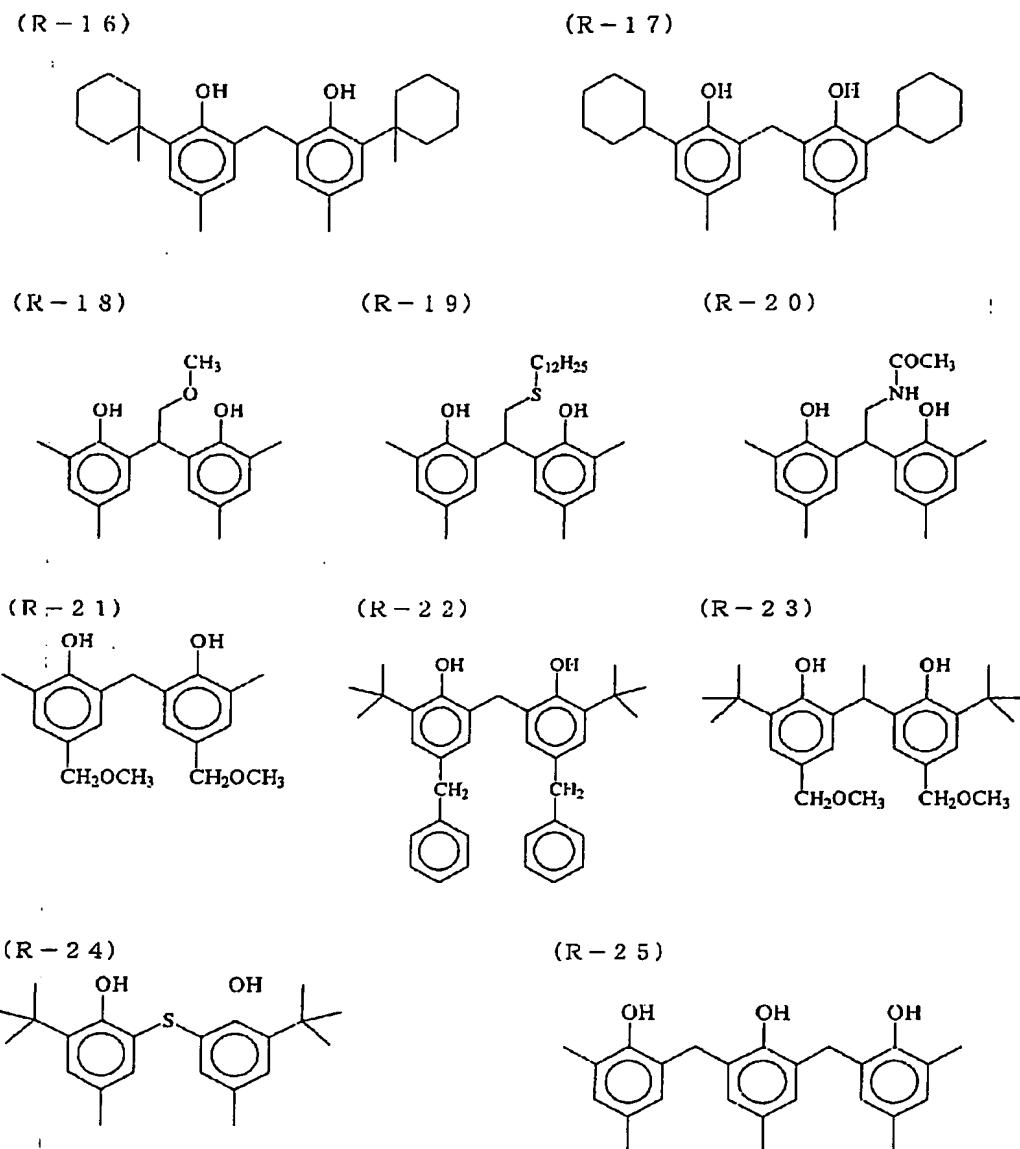
Specific examples of the compounds represented by general formula (R) according to the invention are shown below but the invention is not restricted to them.

[0054]

[Formula 4]

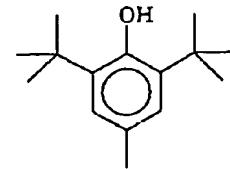
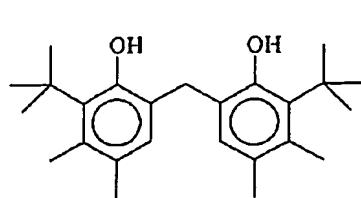
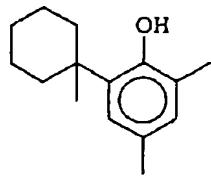


[0055]
[Formula 5]

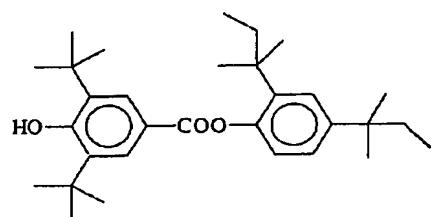
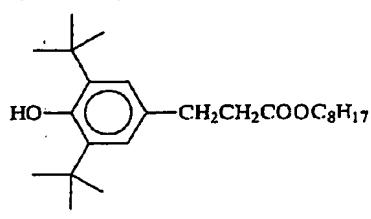


[0056]
 [Formula 6]

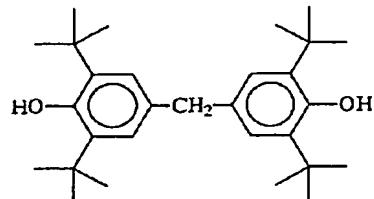
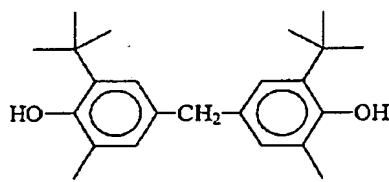
(R - 2 6) (R - 2 7) (R - 2 8)



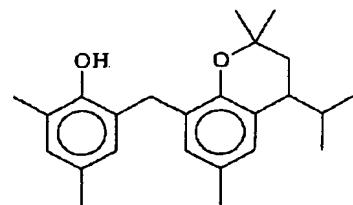
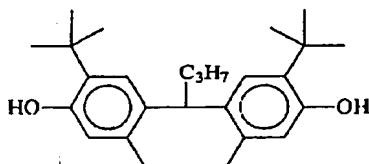
(R - 2 9) (R - 3 0)



(R - 3 1) (R - 3 2)



(R - 3 3) (R - 3 4)



[0057]

As preferred reducing agents of the invention other than those above, there can be mentioned compounds disclosed in JP-A Nos. 2001-188314, 2001-209145, 2001-350235, and 2002-156727.

In the invention, the addition amount of the reducing agent is, preferably, from 0.1 g/m² to 3.0 g/m², more preferably, 0.2 g/m² to 1.5 g/m² and, further preferably 0.3 g/m² to 1.0 g/m². It is, preferably, contained in an amount of 8 mol% to 30 mol%, and more preferably, 10 mol% to 20 mol% per one mol of fatty acid silver in the image forming layer. The reducing agent of the invention is preferably contained in the image forming layer.

[0058]

In the invention, the reducing agent may be incorporated into photosensitive material by being added into the coating solution, such as in the form of a solution, an emulsion dispersion, a solid particle dispersion, and the like.

As a well known emulsion dispersion method, there can be mentioned a method comprising dissolving the thermal solvent in an auxiliary solvent such as oil, for instance, dibutyl phthalate, tricresyl phosphate, glyceryl triacetate, diethyl phthalate, and the like, as well as ethyl acetate, cyclohexanone, and the like; from which an emulsion dispersion is mechanically produced.

[0059]

As solid particle dispersion method, there can be mentioned a method comprising dispersing the powder of the thermal solvent in a proper medium such as water, by means of ball mill, colloid mill, vibrating ball mill, sand mill, jet mill, roller mill, or ultrasonics, thereby obtaining solid dispersion. In this case, there can also be used a protective colloid (such as polyvinyl alcohol), or a surface active agent (for instance, an anionic surface active agent such as sodium triisopropylnaphthalenesulfonate (a mixture of compounds having the isopropyl groups in different substitution sites)). In the mills enumerated above, generally used as the dispersion media are beads made of zirconia and the like, and Zr and the like eluting from the beads may be incorporated in the dispersion. Although depending on the dispersing conditions, the amount of Zr and the like generally incorporated in the dispersion is in a range of from 1 ppm to 1000 ppm. It is practically acceptable so long as Zr is incorporated in an amount of 0.5 mg or less with respect to 1 g of silver.

Preferably, a preservative (for instance, sodium benzoisothiazolinone salt) is added in the water dispersion.

In the invention, furthermore, the reducing agent is preferably used as solid dispersion, and is added in the form of fine particles having average particle size from 0.01 μm to 10 μm , and more preferably, from 0.05 μm to 5 μm and, further preferably, from 0.1 μm to 2 μm . In the invention, other solid dispersions are preferably used with this particle size range.

[0060]

(Description of development accelerator)

In the photothermographic material of the invention, sulfoneamide phenolic compounds represented by the general formula (A) described in the specification of JP-A No. 2000-267222, and specification of JP-A No. 2000-330234, hindered phenolic compound represented by the general formula (II) described in JP-A No. 2001-92075, hydrazine series compounds represented by general formula (I) described in the specification of JP-A No. 10-62895 and the specification of JP-A No. 11-15116, represented by general formula (D) of JP-A No. 2002-156727 and represented by general formula (1) described in the specification of Japanese Patent Application No. 2001-074278, and phenolic or naphthalic compounds represented by general formula (2) described in the specification of JP-A No. 2001-264929 are used preferably as the development accelerator and they are added preferably. The development accelerator described above is used within a range from 0.1 mol% to 20 mol%, preferably, within a range from 0.5 mol% to 10 mol% and, more preferably, within a range from 1 mol% to 5 mol% to the reducing agent. Examples of the introduction method to the photothermographic material can include the same method as those for the reducing agent,

and it is particularly preferred to add as a solid dispersion or an emulsion dispersion. In a case of adding as an emulsion dispersion, it is preferred to add as an emulsion dispersion dispersed by using a high boiling solvent which is solid at a normal temperature and an auxiliary solvent at a low boiling point, or to add as a so-called oilless emulsion dispersion not using the high boiling solvent.

In the present invention, it is more preferred to use, among the development accelerators described above, hydrazine compounds represented by general formula (D) described in the specification of JP-A No. 2002-156727, and phenolic or naphtholic compounds represented by general formula (2) described in the specification of JP-A No. 2001-264929.

[0061]

Particularly preferred development accelerators of the invention are compounds represented by the following general formulae (A-1) and (A-2).

General formula (A-1)



(in which Q_1 represents an aromatic group or heterocyclic group coupling at a carbon atom to $-\text{NHNH}-Q_2$ and Q_2 represents a carbamoyl group, acyl group, alkoxy carbonyl group, aryloxy carbonyl group, sulfonyl group or sulfamoyl group).

[0062]

In general formula (A-1), the aromatic group or heterocyclic group represented by Q_1 is, preferably, 5 to 7 membered unsaturated rings. Preferred examples are benzene ring, pyridine ring, pyrazine ring, pyrimidine ring, pyridazine ring, 1,2,4-triazine ring, 1,3,5-triazine ring, pyrrole ring, imidazole ring, pyrazole ring, 1,2,3-triazole ring, 1,2,4-triazole ring, tetrazole ring, 1,3,4-thiadiazole ring, 1,2,4-thiadiazole ring, 1,2,5-thiadiazole ring, 1,3,4-oxadiazole ring, 1,2,4-oxadiazole ring, 1,2,5-oxadiazole ring, thiazole ring, oxazole ring, isothiazole ring, isooxazole ring, and thiophene ring. Condensed rings in which the rings described above are condensed to each other are also preferred.

[0063]

The rings described above may have substituents and in a case where they have two or more substituent groups, the substituents may be identical or different with each other. Examples of the substituents can include halogen atom, alkyl group, aryl group, carboamide group, alkylsulfoneamide group, arylsulfonamide group, alkoxy group, aryloxy group, alkylthio group, arylthio group, carbamoyl group, sulfamoyl group, cyano group, alkylsulfonyl group, arylsulfonyl group, alkoxy carbonyl group, aryloxy carbonyl group and acyl group. In a case where the substituents are groups capable of substituting, they may have further substituents and examples of preferred substituents can include halogen atom, alkyl group, aryl group, carbonamide group, alkylsulfoneamide group, arylsulfoneamide group, alkoxy group, aryloxy group, alkylthio group, arylthio group, acyl group, alkoxy carbonyl group, aryloxy carbonyl group, carbamoyl group, cyano group, sulfamoyl group, alkylsulfonyl group, arylsulfonyl group and acyloxy group.

[0064]

The carbamoyl group represented by Q_2 is a carbamoyl group preferably having 1 to 50 carbon atoms and, more preferably, 6 to 40 carbon atoms, such as not-substituted carbamoyl, methyl carbamoyl, N-ethylcarbamoyl, N-propylcarbamoyl, N-sec-butylcarbamoyl, N-octylcarbamoyl, N-cyclohexylcarbamoyl, N-tert-butylcarbamoyl, N-dodecylcarbamoyl, N-(3-dodecyloxypropyl)carbamoyl, N-octadecylcarbamoyl, N-{3-(2,4-

tert-pentylphenoxy)propyl} carbamoyl, N-(2-hexyldecyl)carbamoyl, N-phenylcarbamoyl, N-(4-dodecyloxyphenyl)carbamoyl, N-(2-chloro-5-dodecyloxycarbonylphenyl)carbamoyl, N-naphthylcarbamoyl, N-3-pyridylcarbamoyl and N-benzylcarbamoyl.

[0065]

The acyl group represented by Q_2 is an acyl group, preferably, having 1 to 50 carbon atoms and, more preferably, 6 to 40 carbon atoms and examples thereof can include formyl, acetyl, 2-methylpropanoyl, cyclohexylcarbonyl, octanoyl, 2-hexyldecanoyl, dodecanoyl, chloroacetyl, trifluoroacetyl, benzoyl, 4-dodecyloxybenzoyl, and 2-hydroxymethylbenzoyl. Alkoxy carbonyl group represented by Q_2 is an alkoxy carbonyl group, preferably of 2 to 50 carbon atoms and, more preferably, 6 to 40 carbon atoms, and examples thereof can include methoxycarbonyl, ethoxycarbonyl, isobutyloxycarbonyl, cyclohexyloxycarbonyl, dodecyloxycarbonyl and benzyloxycarbonyl.

[0066]

The aryloxy carbonyl group represented by Q_2 is an aryloxy carbonyl group, preferably, having 7 to 50 carbon atoms and, more preferably 7 to 40 carbon atoms, and examples thereof can include phenoxy carbonyl, 4-octyloxyphenoxy carbonyl, 2-hydroxymethylphenoxy carbonyl, and 4-dodecyloxyphenoxy carbonyl. The sulfonyl group represented by Q_2 is a sulfonyl group, preferably, of 1 to 50 carbon atoms and, more preferably, 6 to 40 carbon atoms, and examples thereof can include methylsulfonyl, butylsulfonyl, octylsulfonyl, 2-hexadecylsulfonyl, 3-dodecyloxypropylsulfonyl, 2-octyloxy-5-tert-octylphenyl sulfonyl, and 4-dodecyloxyphenyl sulfonyl.

[0067]

The sulfamoyl group represented by Q_2 is sulfamoyl group, preferably, having 0 to 50 carbon atoms, more preferably, 6 to 40 carbon atoms, and examples thereof can include not-substituted sulfamoyl, N-ethylsulfamoyl group, N-(2-ethylhexyl)sulfamoyl, N-decylsulfamoyl, N-hexadecylsulfamoyl, N-{3-(2-ethylhexyloxy)propyl}sulfamoyl, N-(2-chloro-5-dodecyloxycarbonylphenyl)sulfamoyl, and N-(2-tetradecyloxyphenyl)sulfamoyl. The group represented by Q_2 may further have a group mentioned as the example of the substituent of 5 to 7-membered unsaturated ring represented by Q_1 at the position capable of substituting. In a case where the group has two or more substituents, such substituents may be identical or different with each other.

[0068]

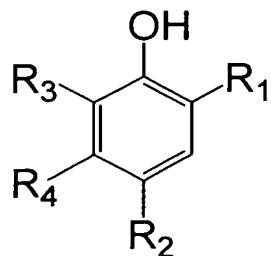
Then, preferred range for the compounds represented by formula (A-1) is to be described. 5 to 6 membered unsaturated ring is preferred for Q_1 , and benzene ring, pyrimidine ring, 1,2,3-triazole ring, 1,2,4-triazole ring, tetrazole ring, 1,3,4-thiadiazole ring, 1,2,4-thiadiazole ring, 1,3,4-oxadiazole ring, 1,2,4-oxadiazole ring, thioazole ring, oxazole ring, isothiazole ring, isooxazole ring and a ring in which the ring described above is condensed with a benzene ring or unsaturated hetero ring are further preferred. Further, Q_2 is preferably a carbamoyl group and, particularly, a carbamoyl group having hydrogen atom on the nitrogen atom is particularly preferred.

[0069]

General formula (A-2)

[0070]

[Formula 7]



[0071]

In general formula (A-2), R₁ represents an alkyl group, acyl group, acylamino group, sulfoneamide group, alkoxycarbonyl group, and carbamoyl group. R₂ represents a hydrogen atom, halogen atom, alkyl group, alkoxy group, aryloxy group, alkylthio group, arylthio group, acyloxy group and carbonate ester group. R₃, R₄ each represent a group capable of substituting for a hydrogen atom on a benzene ring which is mentioned as the example of the substituent for general formula (A-1). R₃ and R₄ may join each other to form a condensed ring.

R₁ is, preferably, an alkyl group having 1 to 20 carbon atoms (for example, methyl group, ethyl group, isopropyl group, butyl group, tert-octyl group, or cyclohexyl group), acylamino group (for example, acetylamino group, benzoylamino group, methylureido group, or 4-cyanophenylureido group), carbamoyl group (for example, n-butylcarbamoyl group, N,N-diethylcarbamoyl group, phenylcarbamoyl group, 2-chlorophenylcarbamoyl group, or 2,4-dichlorophenylcarbamoyl group), acylamino group (including ureido group or urethane group) being more preferred. R₂ is, preferably, a halogen atom (more preferably, chlorine atom, bromine atom), alkoxy group (for example, methoxy group, butoxy group, n-hexyloxy group, n-decyloxy group, cyclohexyloxy group or benzyloxy group), and aryloxy group (phenoxy group or naphthoxy group).

R₃ is, preferably a hydrogen atom, halogen atom or an alkyl group having 1 to 20 carbon atoms, the halogen atom being most preferred. R₄ is preferably a hydrogen atom, alkyl group or an acylamino group, with the alkyl group or the acylamino group being more preferred. Examples of the preferred substituent thereof are identical with those for R₁. In a case where R₄ is an acylamino group, R₄ may preferably be joined with R₃ to form a carbostyryl ring.

[0072]

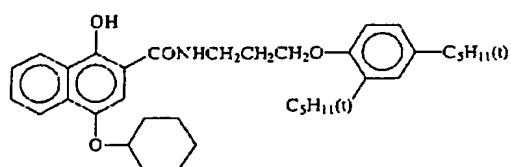
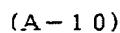
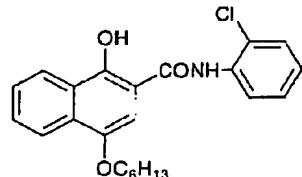
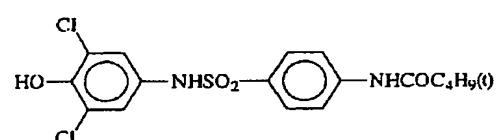
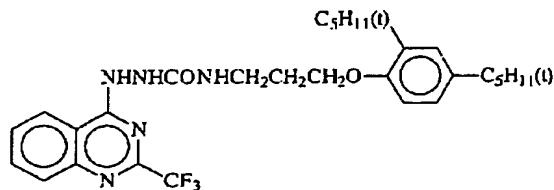
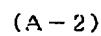
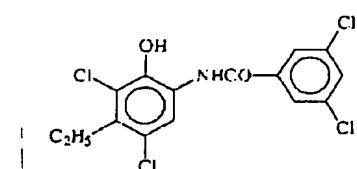
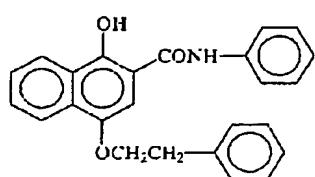
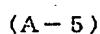
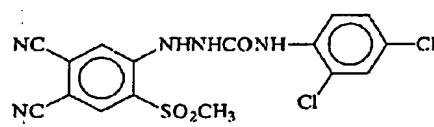
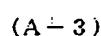
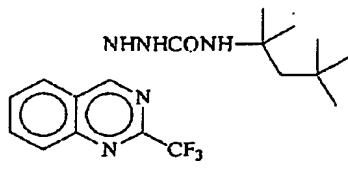
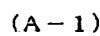
In a case where R₃ and R₄ in general formula (A-2) are joined to each other to form a condensed ring, a naphthalene ring is particularly preferred as the condensed ring. The same substituent as the example of the substituent referred to for general formula (A-1) may be joined to the naphthalene ring. In a case where the general formula (A-2) is a naphtholic compound, R₁ is preferably a carbamoyl group. Among them, benzoyl group is particularly preferred. R₂ is preferably an alkoxy group or aryloxy group and, particularly preferably an alkoxy group.

[0073]

Preferred specific examples for the development accelerator of the invention are to be described below. The invention is not restricted to them.

[0074]

[Formula 8]



[0075]

(Description of hydrogen bonding compound)

When the reducing agent in the invention has aromatic hydroxyl groups (-OH), particularly the aforementioned bisphenols, it is preferred to use in combination, a non-reducing compound having a group capable of forming a hydrogen bond with these groups.

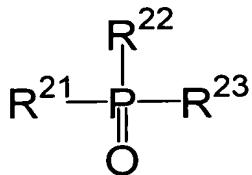
As a group forming a hydrogen bond with a hydroxyl group, there can be mentioned a phosphoryl group, a sulfoxido group, a sulfonyl group, a carbonyl group, an amido group, an ester group, an urethane group, an ureido group, a tertiary amino group, a nitrogen-containing aromatic group, and the like. Particularly preferred among them is phosphoryl group, sulfoxido group, amido group (not having >N-H moiety but being blocked in the form of >N-Ra (where, Ra represents a substituent other than H)), urethane group (not having >N-H moiety but being blocked in the form of >N-Ra (where, Ra represents a substituent other than H)), and ureido group (not having >N-H moiety but being blocked in the form of >N-Ra (where, Ra represents a substituent other than H)).

In the invention, particularly preferred as the hydrogen-bonding compound is the compound expressed by general formula (D) shown below.

General formula (D)

[0076]

[Formula 9]



[0077]

In general formula (D), R²¹ to R²³ each independently represent an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an amino group, or a heterocyclic group, which may be substituted or not substituted.

In the case R²¹ to R²³ contain a substituent, examples of the substituents include a halogen atom, an alkyl group, an aryl group, an alkoxy group, an amino group, an acyl group, an acylamino group, an alkylthio group, an arylthio group, a sulfonamido group, an acyloxy group, an oxycarbonyl group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, a phosphoryl group, and the like, in which preferred as the substituents are an alkyl group or an aryl group, e.g., methyl group, ethyl group, isopropyl group, t-butyl group, t-octyl group, phenyl group, a 4-alkoxyphenyl group, a 4-acyloxyphenyl group, and the like.

Specific examples of an alkyl group expressed by R²¹ to R²³ include methyl group, ethyl group, butyl group, octyl group, dodecyl group, isopropyl group, t-butyl group, t-amyl group, t-octyl group, cyclohexyl group, 1-methylcyclohexyl group, benzyl group, phenetyl group, 2-phenoxypropyl group, and the like.

As aryl groups, there can be mentioned phenyl group, cresyl group, xylyl group, naphthyl group, 4-t-butylphenyl group, 4-t-octylphenyl group, 4-anisidyl group, 3,5-dichlorophenyl group, and the like.

As alkoxy groups, there can be mentioned methoxy group, ethoxy group, butoxy group, octyloxy group, 2-ethylhexyloxy group, 3,5,5-trimethylhexyloxy group, dodecyloxy group, cyclohexyloxy group, 4-methylcyclohexyloxy group, benzyloxy group, and the like.

As aryloxy groups, there can be mentioned phenoxy group, cresyloxy group,

isopropylphenoxy group, 4-t-butylphenoxy group, naphthoxy group, biphenyloxy group, and the like.

As amino groups, there can be mentioned are dimethylamino group, diethylamino group, dibutylamino group, dioctylamino group, N-methyl-N-hexylamino group, dicyclohexylamino group, diphenylamino group, N-methyl-N-phenylamino, and the like.

[0078]

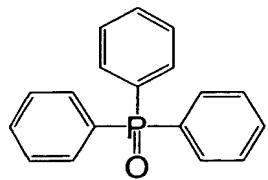
Preferred as R²¹ to R²³ are an alkyl group, an aryl group, an alkoxy group, and an aryloxy group. Concerning the effect of the invention, it is preferred that at least one or more of R²¹ to R²³ are an alkyl group or an aryl group, and more preferably, two or more of them are an alkyl group or an aryl group. From the viewpoint of low cost availability, it is preferred that R²¹ to R²³ are of the same group.

Specific examples of hydrogen bonding compounds represented by general formula (D) of the invention and others are shown below, but it should be understood that the invention is not limited thereto.

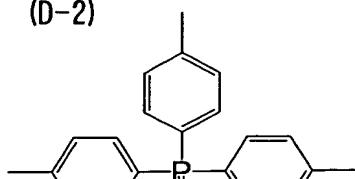
[0079]

[Formula 10]

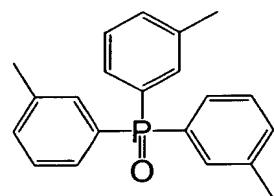
(D-1)



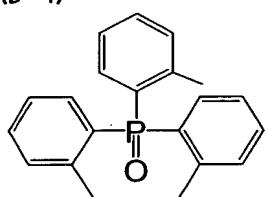
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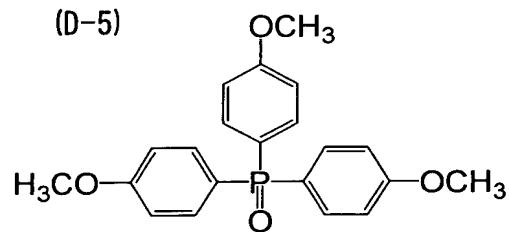
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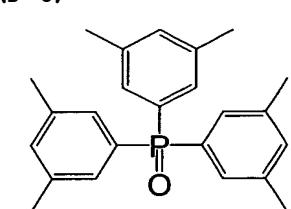
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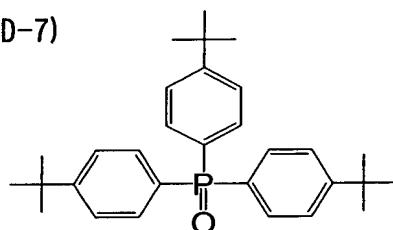
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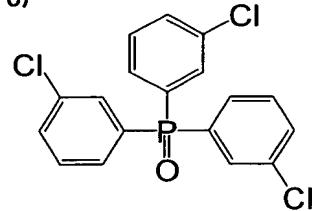
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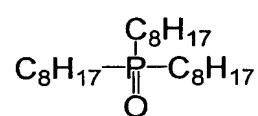
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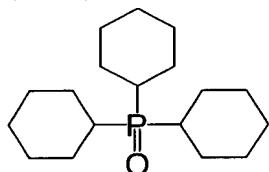
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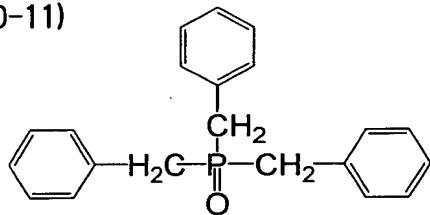
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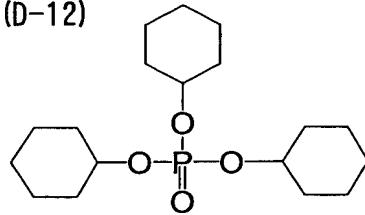
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(D-11)

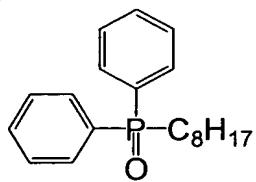


(D-12)

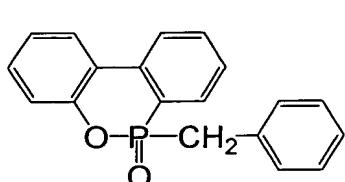


[0080]
[Formula 11]

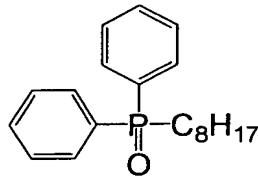
(D-13)



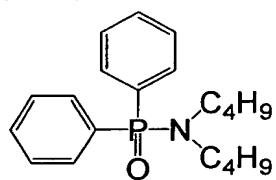
(D-14)



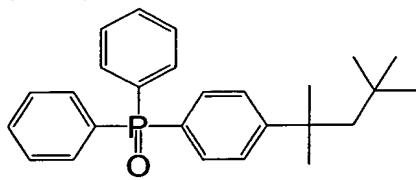
(D-15)



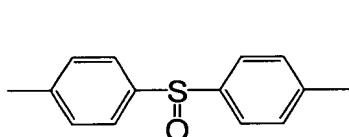
(D-16)



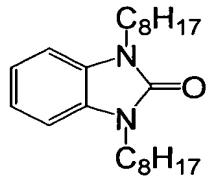
(D-17)



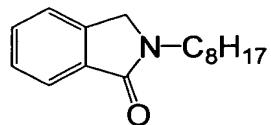
(D-18)



(D-19)



(D-20)



(D-21)



[0081]

Specific examples of hydrogen bonding compounds other than those enumerated above can be found in those described in EP-A No. 1096310 and in Japanese Patent Application Nos. 2000-270498 and 2001-124796.

The compound expressed by general formula (D) used in the invention can be used in the photosensitive material by being incorporated into the coating solution in the form of solution, emulsion dispersion, or solid-dispersed fine particle dispersion similar to the case of reducing agent, however, it is preferred to be used as a solid dispersion. The compound of the invention forms a hydrogen-bonded complex with a compound having a phenolic hydroxyl group and an amino group, and can be isolated as a complex in crystalline state depending on the combination of the reducing agent and the compound expressed by general formula (D) of the invention.

It is particularly preferred to use the crystal powder thus isolated as a solid-dispersed fine particle dispersion, because it provides stable performance. Further, a method in which the reducing agent and the compound expressed by general formula (D) of the invention are mixed in the form of powder and a complex is formed using an

appropriate dispersing agent at the time of dispersion by a sand grinder mill.

The compound expressed by general formula (D) of the invention is preferably used in a range of from 1 to 200 mol%, more preferably from 10 to 150 mol%, and most preferably, from 20 to 100 mol%, with respect to the reducing agent.

[0082]

(Description of silver halide)

1) Halogen composition

For the photosensitive silver halide used in the invention, there is no particular restriction on the halogen composition, and silver chloride, silver bromochloride, silver bromide, silver bromoiodide, silver chlorobromoiode and silver iodide can be used. Among them, silver bromide, silver bromoiodide and silver iodide are preferred. The distribution of the halogen composition in a grain may be uniform or the halogen composition may be changed stepwise, or it may be changed continuously. Further, a silver halide grain having a core/shell structure can be used preferably. The preferred structure is a twofold to fivefold structure and, more preferably, a core/shell grain having a twofold to fourfold structure can be used. Further, a technique of localizing silver bromide or silver iodide to the surface of silver chloride, silver bromide or silver bromochloride grains can also be used preferably.

[0083]

2) Method of grain formation

The method of forming photosensitive silver halide is well-known in the relevant art and, for example, methods described in Research Disclosure No. 10729, June 1978 and USP No. 3700458 can be used. Specifically, a method of preparing a photosensitive silver halide by adding a silver-supplying compound and a halogen-supplying compound in a gelatin or other polymer solution and then mixing them with an organic silver salt is used. Further, a method described in JP-A No. 11-119374 (paragraph Nos. 0217 to 0224) and methods described in JP-A No. 11-352627 and Japanese Patent Application No. 2000-42336 are also preferred.

[0084]

3) Grain size

The grain size of the photosensitive silver halide is preferably small with an aim of suppressing clouding after image formation and, specifically, it is 0.20 μm or less, more preferably, 0.01 μm to 0.15 μm and, further preferably, 0.02 μm to 0.12 μm . The grain size as used herein means an average diameter of a circle converted such that it has the same area as a projection area of the silver halide grain (projection area of a principal plane in the case of a tabular grain).

[0085]

4) Grain shape

Examples of the shape of the silver halide grain can include, for example, a cubic, octahedral, plate-like, spherical, rod-like or potato-like shape. The cubic grain is particularly preferred in the invention. A silver halide grain rounded at corners can also be used preferably. While there is no particular restriction on the index of plane (Mirror's index) of an crystal surface of the photosensitive silver halide grain, it is preferred that the ratio of [100] face is higher, in which the spectral sensitizing efficiency is higher in a case of adsorption of a spectral sensitizing dye. The ratio is preferably 50% or more, more preferably, 65% or more and, further preferably, 80% or more. The ratio of the Mirror's

index [100] face can be determined by the method of utilizing the adsorption dependency of [111] face and [100] face upon adsorption of a sensitizing dye described by T. Tani; in J. Imaging Sci., 29, 165 (1985).

[0086]

5) Heavy metal

In the present invention, a silver halide grain having a hexacyano metal complex on the outermost surface of the grain is preferred. Examples of the hexacyano metal complex include $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Ru}(\text{CN})_6]^{4-}$, $[\text{Os}(\text{CN})_6]^{4-}$, $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Rh}(\text{CN})_6]^{3-}$, $[\text{Ir}(\text{CN})_6]^{3-}$, $[\text{Cr}(\text{CN})_6]^{3-}$, and $[\text{Re}(\text{CN})_6]^{3-}$. In the invention, a hexacyano Fe complex is preferred.

[0087]

Since the hexacyano complex exists in ionic form in an aqueous solution, paired cation is not important and alkali metal ion such as sodium ion, potassium ion, rubidium ion, cesium ion and lithium ion, ammonium ion, alkyl ammonium ion (for example, tetramethyl ammonium ion, tetraethyl ammonium ion, tetrapropyl ammonium ion, and tetra(n-butyl) ammonium ion), which are easily miscible with water and suitable for precipitation operation of a silver halide emulsion are used preferably.

[0088]

The hexacyano metal complex can be added while being mixed with water, as well as a mixed solvent of water and an appropriate organic solvent miscible with water (for example, alcohols, ethers, glycols, ketones, esters and amides) or gelatin.

[0089]

The addition amount of the hexacyano metal complex is preferably from 1×10^{-5} mol to 1×10^{-2} mol and, more preferably, from 1×10^{-4} mol to 1×10^{-3} per one mol of silver in each case.

[0090]

In order to allow the hexacyano metal complex to be present on the outermost surface of a silver halide grain, the hexacyano metal complex is directly added in any stage of: after completion of addition of an aqueous solution of silver nitrate used for grain formation, and before completion of emulsion forming step prior to a chemical sensitization step, of conducting chalcogen sensitization such as sulfur sensitization, selenium sensitization and tellurium sensitization or noble metal sensitization such as gold sensitization; during washing step; during dispersion step; and before chemical sensitization step. In order not to grow the fine silver halide grain, the hexacyano metal complex is rapidly added preferably after the grain is formed, and it is preferably added before completion of the emulsion forming step.

[0091]

Addition of the hexacyano complex may be started after addition of 96 % by mass of an entire amount of silver nitrate to be added for grain formation, more preferably started after addition of 98 % by mass and, particularly preferably, started after addition of 99 % by mass.

[0092]

When any of the hexacyano metal complexes is added after addition of an aqueous silver nitrate just before completion of grain formation, it can be adsorbed to the outermost surface of the silver halide grain and most of them forms an insoluble salt with silver ions on the surface of the grain. Since the hexacyano iron (II) silver salt is a less soluble salt than AgI, re-dissolution with fine grain can be prevented and fine silver halide grain with smaller grain size can be prepared.

[0093]

The photosensitive silver halide grain of the invention can contain metals or complexes of metals belonging to groups 8 to 10 of the periodical table (showing groups 1 to 18). The metal or the center metal of the metal complex in the groups 8 to 10 of the periodical table is preferably rhodium, ruthenium or iridium. The metal complex may be used alone, or two or more kinds of complexes comprising identical or different species of metals may be used together. A preferred content is within a range from 1×10^{-9} mol to 1×10^{-3} mol per one mol of silver. The heavy metals, metal complexes and the addition method thereof are described in JP-A No. 7-225449, JP-A No. 11-65021 (paragraph Nos. 0018 to 0024) and JP-A No. 11-119374 (paragraph Nos. 0227 to 0240).

[0094]

Metal atoms that can be contained in the silver halide grain used in the invention (for example, $[\text{Fe}(\text{CN})_6]^{4-}$), a desalting method of a silver halide emulsion and a chemical sensitization method are described in JP-A No. 11-84574 (paragraph Nos. 0046 to 0050), JP-A No. 11-65021 (paragraph Nos. 0025 to 0031), and JP-A No. 11-119374 (paragraph Nos. 0242 to 0250).

[0095]

6) Gelatin

As the gelatin contained in the photosensitive silver halide emulsion used in the invention, various kinds of gelatins can be used. It is necessary to maintain an excellent dispersion state of a photosensitive silver halide emulsion in an organic silver salt-containing coating solution, and gelatin having a molecular weight of 10000 to 1000000 is used preferably. Further, substituent groups of the gelatin are preferably phthalated. These gelatins may be used upon grain formation or at the time of dispersion after desalting treatment, and it is preferably used during grain formation.

[0096]

7) Sensitizing dye

As the sensitizing dye applicable in the invention, those capable of spectrally sensitizing silver halide grains in a desired wavelength region upon adsorption to silver halide grains having spectral sensitivity suitable for spectral characteristics of an exposure light source can be selected advantageously. The sensitizing dyes and the addition method are disclosed, for example, in JP-A No. 11-65021 (paragraph Nos. 0103 to 0109), a compound represented by the general formula (II) in JP-A No. 10-186572, dyes represented by the general formula (I) in JP-A No. 11-119374 (paragraph No. 0106), dyes described in USP Nos. 5510236 and 3871887 (Example 5), dyes disclosed in JP-A Nos. 2-96131 and 59-48753, as well as page 19, line 38 to page 20, line 35 of EP-A No. 0803764A1, and in Japanese Patent Application Nos. 2001-272747, 2001-290238 and 2002-23306. The sensitizing dyes described above may be used alone or two or more of them may be used in combination. The sensitizing dye is added into the silver halide emulsion preferably within a period after desalting step to coating step and, more

preferably, in a period after desalting to the completion of chemical ripening.

In the invention, the sensitizing dye may be added at any amount according to the property of photosensitivity and fogging, but it is preferably added from 1×10^{-6} mol to 1 mol, and more preferably, from 1×10^{-4} mol to 1×10^{-1} mol per one mol of silver in each case.

[0097]

A supersensitizer can be used in the invention in order to improve spectral sensitization efficiency. Examples of the supersensitizer include compounds described in EP-A No. 587338, U.S. Patent Nos. 3877493 and 4873184, and JP-A Nos. 5-341432, 11-109547 and 10-111543.

[0098]

8) Chemical sensitization

The photosensitive silver halide grain in this invention is preferably chemically sensitized by sulfur sensitization method, selenium sensitization method or tellurium sensitization method. Known compounds, for example, compounds described in JP-A No. 7-128768 and the like can be used as compounds favorable for use in the sulfur sensitization method, the selenium sensitization method and the tellurium sensitization method. The tellurium sensitization method is particularly preferable in the invention, and compounds described in paragraph No. 0030 of JP-A No. 11-65021, and compounds expressed by general formulae (II), (III) and (IV) of JP-A No. 5-313284 are more preferable.

[0099]

The photosensitive silver halide grain in the invention is preferably chemically sensitized by a combination of a gold sensitization method and a chalcogen sensitization method, or by the gold sensitization method alone. A gold sensitizer preferably has a valence of gold of +1 or +3, and generally used gold compounds are preferable as the gold sensitizer. Typical examples thereof include chloroauric acid, bromoauric acid, potassium chloroaurate, potassium broroaurate, auric trichloride, potassium auric thiocyanate, potassium iodoaurate, tetracyanoauricacide, ammonium aurithiocyanate, pyridyltrichloro gold, and the like. Further, gold sensitizers described in U.S. Patent No. 5858637 and Japanese Patent Application No. 2001-79450 also are preferably used.

[0100]

In the invention, chemical sensitization can be applied at any time so long as it is after grain formation and before coating, and it can be applied, after desalting, (1) before spectral sensitization, (2) simultaneously with spectral sensitization, (3) after spectral sensitization and (4) just before coating.

Although the amount of a sulfur sensitizer, a selenium sensitizer and a tellurium sensitizer used in the invention may vary depending on the silver halide grain used, the chemical ripening condition and the like, these sensitizers are used in an amount of about 10^{-8} mol to 10^{-2} mol, preferably, 10^{-7} mol to 10^{-3} mol per one mol of the silver halide.

The amount of the gold sensitizer added may vary depending on various conditions, and it is generally about 10^{-7} mol to 10^{-3} mol and, more preferably, 10^{-6} mol to 5×10^{-4} mol per one mol of the silver halide.

There is no particular restriction on the condition for the chemical sensitization in the invention and, appropriately, pH is 5 to 8, pAg is 6 to 11, and the temperature is 40°C to 95°C.

In the silver halide emulsion used in the invention, a thiosulfonic acid compound may be added by the method shown in EP-A No. 293917.

[0101]

A reduction sensitizer is preferably used for the photosensitive silver halide grain in the invention. As the specific compound for the reduction sensitization, ascorbic acid and thiourea dioxide are preferred, as well as use of stannous chloride, aminoimino methane sulfonic acid, hydrazine derivatives, borane compounds, silane compounds and polyamine compounds is preferred. The reduction sensitizer may be added at any stage in the photosensitive emulsion production process from crystal growth to the preparation step just before coating. Further, it is preferred to apply reduction sensitization by ripening while keeping pH to 7 or higher and pAg to 8.3 or lower for the emulsion, and it is also preferred to apply reduction sensitization by introducing a single addition portion of silver ions during grain formation.

[0102]

The photosensitive silver halide emulsion in the invention preferably contains an FED sensitizer (Fragmentable Electron Donating Sensitizer) as a compound generating two electrons by one photon. As the FED sensitizer, those compounds described in USP Nos. 5747235, 5747236, 6054260 and 5994051, and Japanese Patent Application No. 2001-86161 are preferred. The FED sensitizer may be added preferably at any stage in the photosensitive emulsion production process from the crystal growth to the preparation step just before coating. The addition amount may vary depending on various conditions and as a standard, it is about from 10^{-7} mol to 10^{-1} mol, more preferably, 10^{-6} mol to 5×10^{-2} mol per one mol of the silver halide.

[0103]

9) Combined use of a plurality of silver halides

The photosensitive silver halide emulsion in the photosensitive material used in the invention may be used alone, or two or more kinds of them (for example, those of different average particle sizes, different halogen compositions, different crystal habits and of different conditions for chemical sensitization) may be used together. Gradation can be controlled by using plural kinds of photosensitive silver halides of different sensitivity. The relevant techniques can include those described, for example, in JP-A Nos. 57-119341, 53-106125, 47-3929, 48-55730, 46-5187, 50-73627, and 57-150841. It is preferred to provide a sensitivity difference of 0.2 logE or more between each of the emulsions.

[0104]

10) Coating amount

The addition amount of the photosensitive silver halide, when expressed by the coating amount of silver per one m^2 of the photosensitive material, is preferably from 0.03 g/ m^2 to 0.6 g/ m^2 , more preferably, 0.05 g/ m^2 to 0.4 g/ m^2 and, further preferably, 0.07 g/ m^2 to 0.3 g/ m^2 . The photosensitive silver halide is used in an amount of preferably 0.01 mol to 0.5 mol, more preferably 0.02 mol to 0.3 mol, and further more preferably 0.03 mol to 0.2 mol per one mol of the organic silver salt.

[0105]

11) Mixing silver halide and organic silver salt

Examples of methods and conditions for mixing the silver halide and the organic silver salt separately prepared include a method of mixing a separately prepared

photosensitive silver halide and an organic silver salt by a high speed stirrer, ball mill, sand mill, colloid mill, vibration mill, or homogenizer, or a method of mixing a photosensitive silver halide completed for preparation at any timing in the preparation of an organic silver salt and preparing the organic silver salt. However, the method is not particularly limited as long as the effect of the invention is obtained. Further, mixing two or more types of aqueous dispersions of organic silver salts with two or more types of aqueous dispersions of photosensitive silver salts is preferable for controlling photographic characteristics.

[0106]

12) Mixing silver halide into coating solution

In the invention, the time of adding silver halide to the coating solution for the image forming layer is preferably in the range from 180 minutes before to just prior to the coating, more preferably, 60 minutes before to 10 seconds before coating. But there is no restriction on mixing methods and mixing conditions as far as the effect of the invention appears sufficient. As an embodiment of a mixing method, there is a method of mixing in the tank controlling the average residence time desired. The average residence time herein is calculated from addition flux and the amount of solution transferred to the coater. Another embodiment of mixing method is a method using a static mixer, which is described in 8th edition of "Ekitai kongou gijutsu" by N. Harnby and M. F. Edwards, translated by Kouji Takahashi (Nikkankougyou shinbunsha, 1989).

[0107]

(Descriprion of binder)

Any type of polymer may be used as the binder for the organic silver salt-containing layer of the invention. Suitable as the binder are those that are transparent or translucent, and that are generally colorless, such as natural resin or polymer and their copolymers; synthetic resin or polymer and their copolymer; or media forming a film; for example, included are gelatin, rubber, poly (vinyl alcohol), hydroxyethyl cellulose, cellulose acetate, cellulose acetate butyrate, poly (vinyl pyrrolidone), casein, starch, poly(acrylic acid), poly(methylmethacrylic acid), poly(vinyl chloride), poly(methacrylic acid), styrene-maleic anhydride copolymers, styrene-acrylonitrile copolymers, styrene-butadiene copolymers, poly(vinyl acetal)(e.g., poly(vinyl formal) and poly(vinyl butyral)), poly(ester), poly(urethane), phenoxy resin, poly(vinylidene chloride), poly(epoxide), poly(carbonate), poly(vinyl acetate), poly(olefin), cellulose esters, and poly(amide). The binder may be mixed with water or an organic solvent or may be formed as an emulsion for coating.

[0108]

In the invention, the glass transition temperature (which may be occasionally referred to as "Tg" hereinafter) of the binder which can be used together with the layer containing the organic silver salt is preferably 0 to 80°C, more preferably 10 to 70°C, and further more preferably 15 to 60°C.

[0109]

In the specification, Tg was calculated according to the following equation.

$$1/Tg = \Sigma(Xi/Tgi)$$

Where, the polymer is obtained by copolymerization of n monomer compounds (from i=1 to i=n); Xi represents the mass fraction of the ith monomer ($\Sigma Xi=1$), and Tgi is the glass transition temperature (absolute temperature) of the homopolymer obtained with the ith monomer. The symbol Σ stands for the summation from i=1 to i=n. Values for

the glass transition temperature (Tgi) of the homopolymers derived from each of the monomers were obtained from J. Brandrup and E.H. Immergut, Polymer Handbook (3rd Edition)(Wiley-Interscience, 1989).

[0110]

If necessary, two or more binders may be used. Further, a binder having a glass transition temperature of 20°C or more and a binder having a glass transition temperature of less than 20°C may be used in combination. When two or more types of polymers having different Tgs are blended for use, the weight-average Tgs of the polymers are preferably within the aforementioned range.

[0111]

In the invention, the layer containing organic silver salt is preferably formed by first applying a coating solution containing 30 % by mass or more of water in the solvent and by then drying the coating solution.

In the invention, in the case the layer containing organic silver salt is formed by first applying a coating solution containing 30% by mass or more of water in the solvent and by then drying, and furthermore, in the case the binder of the layer containing organic silver salt is soluble or dispersible in an aqueous solvent (water solvent), the performance can be ameliorated particularly in the case a polymer latex having an equilibrium water content of 2% by mass or lower at 25°C and 60%RH is used. Most preferred embodiment is such prepared to yield an ion conductivity of 2.5 mS/cm or lower, and as such a preparation method, there can be mentioned a refining treatment using a separation function membrane after synthesizing the polymer.

[0112]

The aqueous solvent in which the polymer is soluble or dispersible, as referred to herein, signifies water or water containing 70 % by mass or less of a water-admixing organic solvent mixed therein. As water-admixing organic solvents, there can be mentioned, for example, alcohols such as methyl alcohol, ethyl alcohol, propyl alcohol, and the like; cellosolves such as methyl cellosolve, ethyl cellosolve, butyl cellosolve, and the like; ethyl acetate, dimethylformamide, and the like.

[0113]

The term “equilibrium water content at 25°C and 60%RH” as referred to herein can be expressed as follows:

Equilibrium water content at 25°C and 60%RH

$$= [(W_1 - W_0)/W_0] \times 100 \text{ (% by mass)}$$

where, W1 is the weight of the polymer in moisture-controlled equilibrium under the atmosphere of 25°C and 60%RH, and W0 is the absolutely dried weight of the polymer at 25°C.

[0114]

For the definition and the method of measurement for water content, reference can be made to Polymer Engineering Series 14, “Testing methods for polymeric materials” (The Society of Polymer Science, Japan, published by Chijin Shokan).

[0115]

The equilibrium water content of the binder polymer of the invention at 25°C and 60%RH is preferably 2% by mass or lower, but is more preferably, 0.01% by mass to 1.5%

by mass, and is most preferably, 0.02% by mass to 1% by mass.

[0116]

In the invention, a polymer dispersible in an aqueous solvent is particularly preferable. Examples of dispersed states may include a latex, in which water-insoluble fine particles of hydrophobic polymer are dispersed, or such in which polymer molecules are dispersed in molecular states or by forming micelles, but preferred are latex-dispersed particles. The average particle size of the dispersed particles is in a range of from 1 to 50,000 nm, preferably 5 nm to 1,000 nm, more preferably, 10 nm to 500 nm, and most preferably, 50 nm to 200 nm. There is no particular limitations concerning particle size distribution of the dispersed particles, and the dispersed particles may be widely distributed or may exhibit a monodisperse particle size distribution. From the viewpoint of controlling the physical properties of the coating solution, preferred mode of usage includes mixing two or more types of particles each having monodisperse particle distribution.

[0117]

In the invention, preferred embodiment of the polymers capable of being dispersed in an aqueous solvent includes hydrophobic polymers such as acrylic polymers, poly(ester), rubber (e.g., SBR resin), poly(urethane), poly(vinyl chloride), poly(vinyl acetate), poly(vinylidene chloride), poly(olefin), and the like. As the polymers above, usable are straight chain polymers, branched polymers, or crosslinked polymers; also usable are so-called homopolymers in which single monomer is polymerized, or copolymers in which two or more types of monomers are polymerized. In the case of a copolymer, it may be a random copolymer or a block copolymer. The molecular weight of these polymers is, in number average molecular weight, in a range of from 5,000 to 1,000,000, preferably from 10,000 to 200,000. Those having too small molecular weight exhibit insufficient mechanical strength on forming the image forming layer, and those having too large molecular weight are also not preferred because the filming properties are poor. Further, crosslinking polymer latexes are particularly preferred for use.

[0118]

(Specific examples of latex)

Specific examples of preferred polymer latexes are given below, which are expressed by the starting monomers with % by mass given in parenthesis. The molecular weight is given in number average molecular weight. In the case a polyfunctional monomer is used, the concept of molecular weight is not applicable because they build a crosslinked structure. Hence, they are denoted as "crosslinking", and the molecular weight is omitted. Tg represents glass transition temperature.

[0119]

P-1; Latex of -MMA(70)-EA(27)-MAA(3)- (molecular weight 37000, Tg 61°C)
P-2; Latex of -MMA(70)-EHA(20)-St(5)-AA(5)- (molecular weight 40000, Tg

59 °C)

P-3; Latex of -St(50)-Bu(47)-MAA(3)- (crosslinking, Tg -17°C)
P-4; Latex of -St(68)-Bu(29)-AA(3)- (crosslinking, Tg 17°C)
P-5; Latex of -St(71)-Bu(26)-AA(3)- (crosslinking, Tg 24°C)
P-6; Latex of -St(70)-Bu(27)-IA(3)- (crosslinking)
P-7; Latex of -St(75)-Bu(24)-AA(1)- (crosslinking, Tg 29°C)
P-8; Latex of -St(60)-Bu(35)-DVB(3)-MAA(2)- (crosslinking)

P-9; Latex of -St(70)-Bu(25)-DVB(2)-AA(3)- (crosslinking)
P-10; Latex of -VC(50)-MMA(20)-EA(20)-AN(5)-AA(5)- (molecular weight
80000)
P-11; Latex of -VDC(85)-MMA(5)-EA(5)-MAA(5)- (molecular weight 67000)
P-12; Latex of -Et(90)-MAA(10)- (molecular weight 12000)
P-13; Latex of -St(70)-2EHA(27)-AA(3)- (molecular weight 130000, Tg 43°C)
P-14; Latex of -MMA(63)-EA(35)-AA(2)- (molecular weight 33000, Tg 47°C)
P-15; Latex of -St(70.5)-Bu(26.5)-AA(3)- (crosslinking, Tg 23°C)
P-16; Latex of -St(69.5)-Bu(27.5)-AA(3)- (crosslinking, Tg 20.5°C)

[0120]

In the structures above, abbreviations represent monomers as follows. MMA: methyl metacrylate, EA: ethyl acrylate, MAA: methacrylic acid, 2EHA: 2-ethylhexyl acrylate, St: styrene, Bu: butadiene, AA: acrylic acid, DVB: divinylbenzene, VC: vinyl chloride, AN: acrylonitrile, VDC: vinylidene chloride, Et: ethylene, IA: itaconic acid.

[0121]

The polymer latexes above are commercially available, and polymers below are usable. As examples of acrylic polymers, there can be mentioned Cevian A-4635, 4718, and 4601 (all manufactured by Daicel Chemical Industries, Ltd.), Nipol Lx811, 814, 821, 820, and 857 (all manufactured by Nippon Zeon Co., Ltd.), and the like; as examples of poly(ester), there can be mentioned FINETEX ES650, 611, 675, and 850 (all manufactured by Dainippon Ink and Chemicals, Inc.), WD-size and WMS (all manufactured by Eastman Chemical Co.), and the like; as examples of poly(urethane), there can be mentioned HYDRAN AP10, 20, 30, and 40 (all manufactured by Dainippon Ink and Chemicals, Inc.), and the like; as examples of rubber, there can be mentioned LACSTAR 7310K, 3307B, 4700H, and 7132C (all manufactured by Dainippon Ink and Chemicals, Inc.), Nipol Lx416, 410, 438C, and 2507 (all manufactured by Nippon Zeon Co., Ltd.), and the like; as examples of poly(vinyl chloride), there can be mentioned G351 and G576 (all manufactured by Nippon Zeon Co., Ltd.), and the like; as examples of poly(vinylidene chloride), there can be mentioned L502 and L513 (all manufactured by Asahi Chemical Industry Co., Ltd.), and the like; as examples of poly(olefin), there can be mentioned Chemipearl S120 and SA100 (all manufactured by Mitsui Petrochemical Industries, Ltd.), and the like.

[0122]

The polymer latexes above may be used alone, or may be used by blending two or more types depending on needs.

[0123]

(Preferable latex)

Particularly preferred as the polymer latex for use in the invention is that of styrene-butadiene copolymer. The weight ratio of monomer unit for styrene to that of butadiene constituting the styrene-butadiene copolymer is preferably in a range of from 40:60 to 95:5. Further, the monomer unit of styrene and that of butadiene preferably accounts for 60 to 99% by mass with respect to the copolymer. Moreover, the polymer latex of the invention contains acrylic acid or methacrylic acid, preferably, for 1 to 6% by mass, and more preferably, for 2 to 5% by mass, with respect to the total mass of the monomer unit of styrene and that of butadiene. The polymer latex of the invention preferably contains acrylic acid. The preferred range of the molecular weight is the same

as that described above.

[0124]

As the latex of styrene-butadiene copolymer preferably used in the invention, there can be mentioned P-3 to P-8 and P-15, or commercially available LACSTAR-3307B, 7132C, Nipol Lx416, and the like.

[0125]

In the layer containing organic silver salt of the photosensitive material according to the invention, if necessary, there can be added hydrophilic polymers such as gelatin, polyvinyl alcohol, methyl cellulose, hydroxypropyl cellulose, carboxymethyl cellulose, and the like. The hydrophilic polymers above are added in an amount of 30% by mass or less, preferably 20% by mass or less, with respect to the total weight of the binder incorporated in the layer containing organic silver salt.

[0126]

The layer containing organic silver salt (i.e., the image forming layer) of the invention is preferably formed by using the polymer latex. The amount of the binder in the layer containing organic silver salt is set such that the weight ratio of the total binder to the organic silver salt is in a range of 1/10 to 10/1, preferably 1/3 to 5/1, and more preferably 1/1 to 3/1.

[0127]

The layer containing organic silver salt is, in general, a photosensitive layer (emulsion layer) containing a photosensitive silver halide, i.e., the photosensitive silver salt; in such a case, the weight ratio of total binder to silver halide is in a range of from 400 to 5, more preferably, from 200 to 10.

[0128]

The total binder content in the image forming layer of the invention is preferably in a range of from 0.2 g/m² to 30 g/m², more preferably from 1 g/m² to 15 g/m², and most preferably, from 2 g/m² to 10 g/m². In the image forming layer of the invention, there may be added a crosslinking agent for crosslinking, or a surface active agent and the like to improve coating properties.

[0129]

(Preferable solvent for coating solution)

An aqueous solvent containing 30 % by mass or more of water is preferably used as the solvent for a coating solution of the layer containing organic silver salt of the photosensitive material in the invention. (For simplicity, a solvent and a dispersion medium are collectively referred to as the "solvent" herein.) As components other than water, any water-miscible organic solvent such as methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, methyl cellosolve, ethyl cellosolve, dimethylformamide, ethyl acetate, and the like may be used. The water content of the solvent for the coating solution is 50% by mass or more, preferably 70% by mass and more. Examples of a preferable composition for the solvent other than water include water/methyl alcohol (90/10), water/methyl alcohol (70/30), water/methyl alcohol/dimethylformamide (80/15/5), water/methyl alcohol/ethyl cellosolve (85/15/5) and water/methyl alcohol/isopropyl alcohol (85/10/5) (all in % by mass).

[0130]

(Description of antifoggant)

In the invention, the photothermographic material has high developing activity, and such a material is likely to cause fogging. Thus, an antifoggant which prevents fogging without lowering the developing activity is preferably added to the photothermographic material.

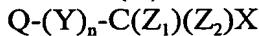
As the antifoggant, stabilizer, and stabilizer precursor usable in the invention, there can be mentioned those disclosed as patents in paragraph number 0070 of JP-A No. 10-62899 and in line 57 of page 20 to line 7 of page 21 of EP-A No. 0803764A1, the compounds described in JP-A Nos. 9-281637 and 9-329864, in USP No. 6,083,681, and in EP-A No. 1048975. Furthermore, the antifoggant preferably used in the invention is an organic halogen compound, and those disclosed in paragraph Nos. 0111 to 0112 of JP-A No. 11-65021 can be enumerated as examples thereof. In particular, the organic halogen compound expressed by formula (P) in JP-A No. 2000-284399, the organic polyhalogen compound expressed by formula (II) in JP-A No. 10-339934, and organic polyhalogen compounds described in JP-A Nos. 2001-31644 and 2001-33911 are preferred.

[0131]

1. Description of polyhalogen compound

Organic polyhalogen compounds preferably used in the invention are specifically described below. In the invention, preferred polyhalogen compounds are the compounds expressed by general formula (H) below:

General formula (H)



In general formula (H), Q represents an alkyl group, an aryl group, or a heterocyclic group; Y represents a divalent connecting group; n represents 0 or 1; Z₁ and Z₂ represent a halogen atom; and X represents hydrogen atom or an electron attracting group.

In general formula (H), Q is preferably an aryl group or a heterocyclic group.

In the case Q is a heterocyclic group in general formula (H), it preferably is a nitrogen-containing heterocyclic group having 1 or 2 nitrogen atoms, and particularly preferred are 2-pyridyl group and 2-quinolyl group.

In the case Q is an aryl group in general formula (H), Q preferably is a phenyl group substituted by an electron-attracting group whose Hammett substitution coefficient σ_p yields a positive value. For the details of Hammett substitution coefficient, reference can be made to Journal of Medicinal Chemistry, Vol. 16, No. 11 (1973), pp. 1207 to 1216, and the like. As such electron-attracting groups, examples include, halogen atoms (fluorine atom (σ_p value: 0.06), chlorine atom (σ_p value: 0.23), bromine atom (σ_p value: 0.23), iodine atom (σ_p value: 0.18)), trihalomethyl groups (tribromomethyl (σ_p value: 0.29), trichloromethyl (σ_p value: 0.33), trifluoromethyl (σ_p value: 0.54)), a cyano group (σ_p value: 0.66), a nitro group (σ_p value: 0.78), an aliphatic aryl or heterocyclic sulfonyl group (for example, methanesulfonyl (σ_p value: 0.72)), an aliphatic aryl or heterocyclic acyl group (for example, acetyl (σ_p value: 0.50) and benzoyl (σ_p value: 0.43)), an alkinyl (e.g., C≡CH (σ_p value: 0.23)), an aliphatic aryl or heterocyclic oxycarbonyl group (e.g., methoxycarbonyl (σ_p value: 0.45) and phenoxy carbonyl (σ_p value: 0.44)), a carbamoyl group (σ_p value: 0.36), sulfamoyl group (σ_p value: 0.57), sulfoxido group, heterocyclic group, and phosphoryl group. Preferred range of the σ_p value is from 0.2 to 2.0, and more preferably, from 0.4 to 1.0. Preferred as the electron-attracting groups are carbamoyl group, an alkoxy carbonyl group, an alkylsulfonyl group, and an alkylphosphoryl group, and particularly preferred among them is carbamoyl group.

X preferably is an electron-attracting group, more preferably, a halogen atom, an

aliphatic aryl or heterocyclic sulfonyl group, an aliphatic aryl or heterocyclic acyl group, an aliphatic aryl or heterocyclic oxycarbonyl group, carbamoyl group, or sulfamoyl group; particularly preferred among them is a halogen atom. Among halogen atoms, preferred are chlorine atom, bromine atom, and iodine atom; more preferred are chlorine atom and bromine atom; and particularly preferred is bromine atom.

Y preferably represents $-C(=O)-$, $-SO-$, or $-SO_2-$; more preferably, $-C(=O)-$ or $-SO_2-$; and particularly preferred is $-SO_2-$. n represents 0 or 1, and preferred is 1.

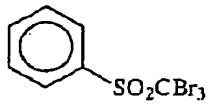
[0132]

Specific examples of the compounds expressed by general formula (H) of the invention are shown below.

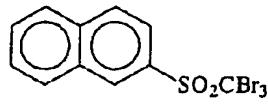
[0133]

[Formula 12]

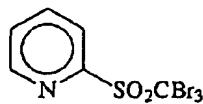
(H - 1)



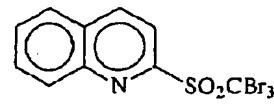
(H - 2)



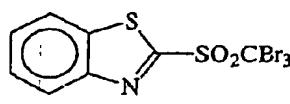
(H - 3)



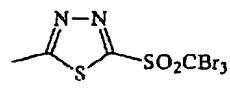
(H - 4)



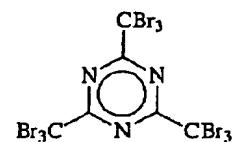
(H - 5)



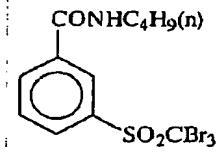
(H - 6)



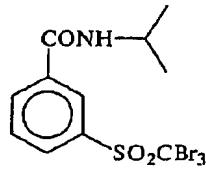
(H - 7)



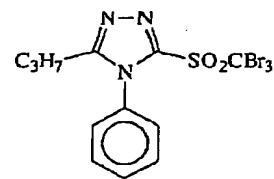
(H - 8)



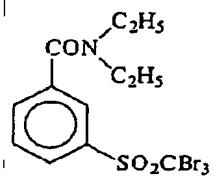
(H - 9)



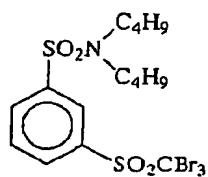
(H - 1 0)



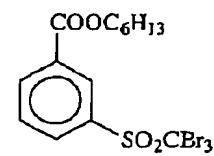
(H - 1 1)



(H - 1 2)

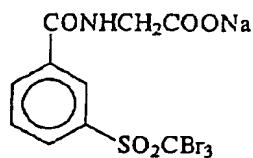


(H - 1 3)

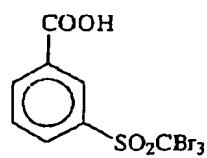


[0134]
[Formula 13]

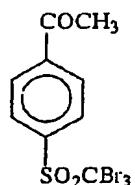
(H - 1 4)



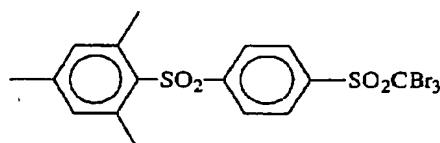
(H - 1 5)



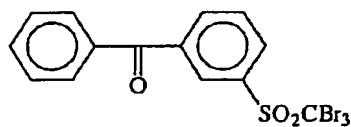
(H - 1 6)



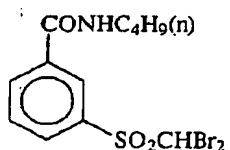
(II - 1 7)



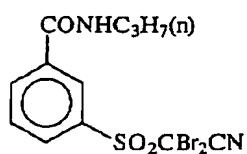
(H - 1 8)



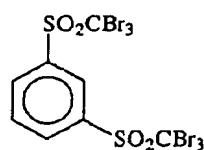
(H - 1 9)



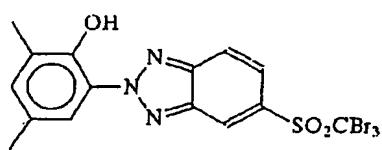
(H - 2 0)



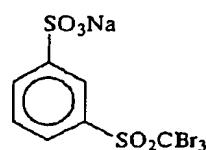
(H - 2 1)



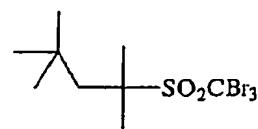
(H - 2 2)



(H - 2 3)



(H - 2 4)



[0135]

As preferred polyhalogen compounds of the invention other than those above, there can be mentioned compounds disclosed in JP-A Nos. 2001-31644, 2001-56526, and 2001-209145.

The compounds expressed by general formula (H) of the invention are preferably used in an amount of from 10^{-4} mol to 1 mol, more preferably, 10^{-3} mol to 0.5 mol, and most preferably, 1×10^{-2} mol to 0.2 mol, per one mol of non-photosensitive silver salt incorporated in the image forming layer.

In the invention, usable methods for incorporating the antifoggant into the photosensitive material are those described above in the method for incorporating the reducing agent; similarly, for the organic polyhalogen compound, it is preferably added in the form of a solid particle dispersion.

[0136]

2. Other antifoggants

As other antifoggants, there can be mentioned a mercury (II) salt described in paragraph number 0113 of JP-A No. 11-65021, benzoic acids described in paragraph number 0114 of the same literature, a salicylic acid derivative described in JP-A No. 2000-206642, a formaline scavenger compound expressed by general formula (S) in JP-A No. 2000-221634, a triazine compound related to Claim 9 of JP-A No. 11-352624, a compound expressed by general formula (III), 4-hydroxy-6-methyl-1,3,3a, 7-tetrazaindene and the like, as described in JP-A No. 6-11791.

[0137]

The photothermographic material of the invention may further contain an azonium salt in order to prevent fogging. As azonium salts, there can be mentioned a compound expressed by general formula (XI) as described in JP-A No. 59-193447, a compound described in JP-B No. 55-12581, and a compound expressed by general formula (II) in JP-A No. 60-153039. The azonium salt may be added to any part of the photosensitive material, but as the addition layer, preferred is to select a layer on the side having thereon the photosensitive layer, and more preferred is to select a layer containing organic silver salt. The azonium salt may be added at any time of the process of preparing the coating solution; in the case the azonium salt is added into the layer containing the organic silver salt, any time of the process may be selected, from the preparation of the organic silver salt to the preparation of the coating solution, but preferred is to add the salt after preparing the organic silver salt and just before the coating. As the method for adding the azonium salt, any method using a powder, a solution, a fine-particle dispersion, and the like, may be used. Furthermore, it may be added as a solution having mixed therein other additives such as sensitizing agents, reducing agents, tone adjusting agents, and the like. In the invention, the azonium salt may be added at any amount, but preferably, it is added in a range of from 1×10^{-6} mol to 2 mol, and more preferably, from 1×10^{-3} mol to 0.5 mol per one mol of silver.

[0138]

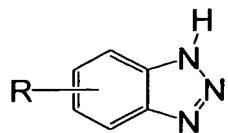
(Benzotriazole Compound)

1) Benzotriazole Compound Represented by General Formula (1)

It is preferred that the photothermographic material of the present invention contains the benzotriazole compound described in the following general formula (1).

[0139]

[Formula 14]



[0140]

In general formula (1), R represents a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, an aryl group, a halogen atom, an amino group, a nitro group, an alkoxy carbonyl group, a substituted or unsubstituted carboxylic acid group or a salt thereof and a sulfonic acid group or a salt thereof.

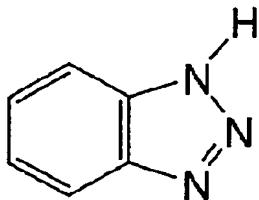
Examples of an alkyl group having 1 to 4 carbon atoms represented by R include a methyl group, an ethyl group and a butyl group. Examples of an aryl group include a phenyl group and so on. Examples of a halogen atom include a chlorine atom and a bromine atom and so on. Examples of a salt of carboxylic acid group or a sulfonic acid group include alkaline metal salts, e.g., a sodium salt, a potassium salt and the like.

[0141]

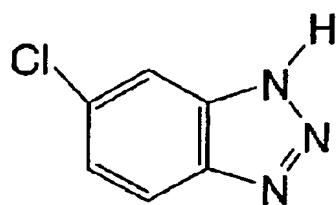
Specific examples of a compound represented by general formula (1) used in the present invention are set forth below, however, the compound used in the present invention is not limited thereto.

[Formula 15]

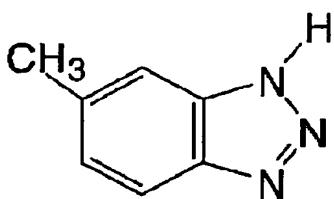
1-1



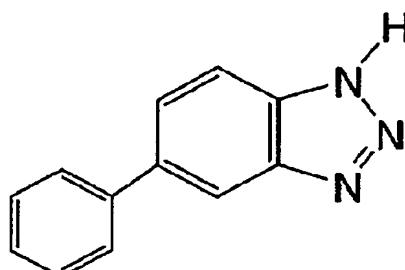
1-2



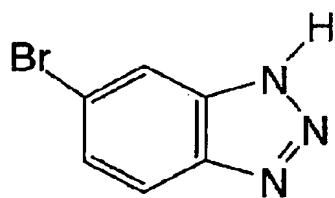
1-3



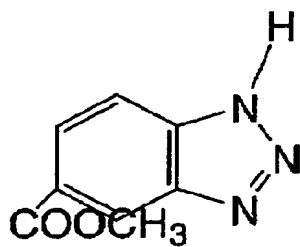
1-4



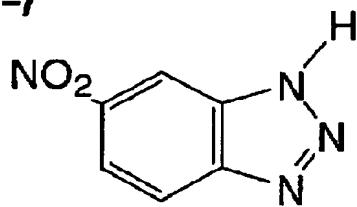
1-5



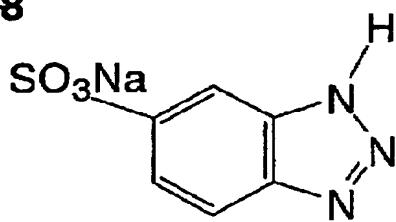
1-6



1-7



1-8



[0142]

The compound represented by general formula (1) can be added to any layer as long as the layer is located on the side of the image forming layer with respect to the support. Most preferably, the compound is added to the layer containing the photosensitive silver halide (hereafter this layer will be described as "the image forming layer") or the layer adjacent to the image forming layer.

In order to add the compound represented by general formula (1) in these layers, the compound is dissolved in the coating solution directly or in the solvent, e.g., water, metylethylketone (MEK), alcohols and the like.

The addition amount of the compound represented by general formula (1) is from 10^{-4} mol to 1 mol per one mol of total silver, preferably from 10^{-3} mol to 0.1 mol per one mol of total silver.

[0143]

One type of the compound represented by general formula (1) may be added, or two or more types of the compound may be added.

[0144]

2) Benzotriazole Compound Represented by General Formula (2)

It is preferred that the photothermographic material of the present invention contains the sulfonylbenzotriazole compound described in the following general formula (2).

[0145]

General formula (2)

[Formula 16]



[0146]

R represent an alkyl group or an alkenyl group having 20 or less carbon atoms, preferably an alkyl group or an alkenyl group having 10 or less carbon atoms, more preferably an alkyl group or an alkenyl group having 5 or less carbon atoms; an aryl group, an alkaryl group or an aralkyl group having 20 or less carbon atoms, preferably an aryl group, an alkaryl group or an aralkyl group having 10 or less carbon atoms, more preferably an aryl group, an alkaryl group or an aralkyl group having 6 or less carbon atoms; an aliphatic or an aromatic hetero ring group having 6 or less ring atoms; and a carbon ring group having 6 or less carbon atoms.

[0147]

R can further have a substituent itself. In the case where R is an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group, an alkaryl group, an alarkyl group and an aliphatic or an aromatic hetero ring group, these groups can have further substituent. Non-limited typical examples include an alkyl group (e.g., a methyl group, an ethyl group, a propyl group, an iso-propyl group and so on); a halogen atom (e.g., fluorine, chlorine, bromine and iodine); an alkoxy or an aryloxy group (e.g., a methoxy group, an ethoxy group, a phenoxy group and so on); a nitro group, a cyano group, an alkylsulfonyl group, or an arylsulfonyl group and so on. These kinds of subsutituent and these synthetic methods are known among the people having general knowledge about organic chemistry. It is common particularly when R is an aryl group such as a phenyl group.

[0148]

Benzotriazole can have a substituent itself. Non-limited typical examples include an alkyl group (e.g., a methyl group, an ethyl group, a propyl group, an iso-propyl group and so on); a halogen atom (e.g., fluorine, chlorine, bromine and iodine); an alkoxy

or an aryloxy group (e.g., a methoxy group, an ethoxy group, a phenoxy group and so on); a nitro group, a cyano group, an alkylsulfonyl group, or an arylsulfonyl group and so on. These kinds of substituent and these synthetic methods are well known among the people having general knowledge about organic chemistry.

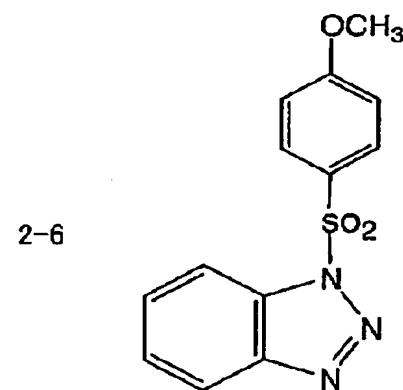
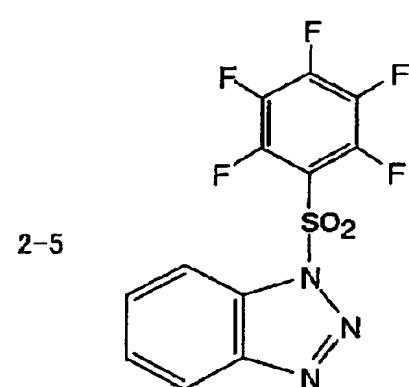
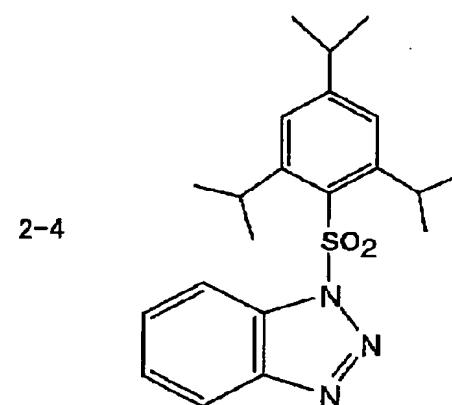
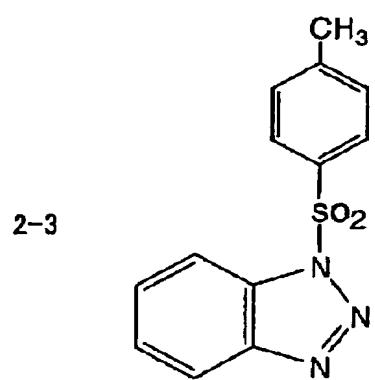
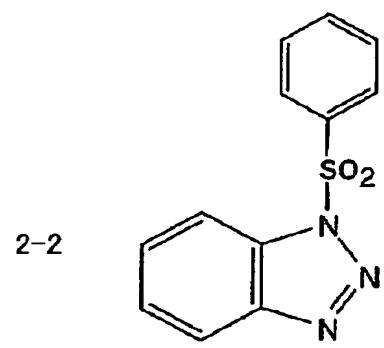
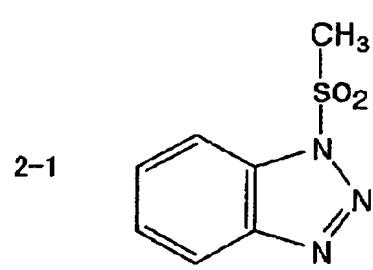
[0149]

Preferred compounds represented by above general formula (2) are the compounds where R is an aryl group such as a phenyl group or a substituted phenyl group and so on.

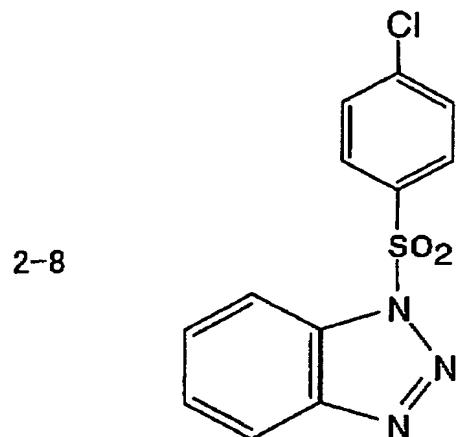
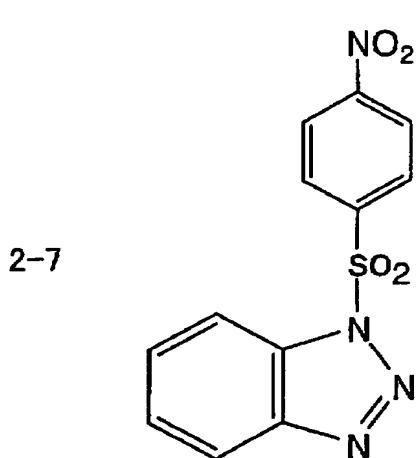
[0150]

Specific examples of the compound represented by general formula (2) are set forth below, however, the compound used in the present invention is not limited thereto.

[Formula 17]



[0151]
[Formula 18]



[0152]

The compound represented by general formula (2) can be added to any layer as long as it is located on the side of the image forming layer with respect to the support, most preferably to the layer containing the photosensitive silver halide or the layer adjacent to the image forming layer.

In order to add the compound represented by general formula (2) in these layers, the compound is dissolved in the coating solution directly or with the solvent, e.g., water, metylethylketone (MEK), alcohols and the like.

The addition amount of the compound represented by general formula (2) is from 10⁻⁴ mol to 1 mol per one mol of total silver, preferably from 10⁻³ mol to 0.1 mol per one mol of total silver.

[0153]

Either only one or more than two kinds of the compound represented by general formula (2) can be added. Further more, the compound represented by general formula (2) can be added individually or together with the compound represented by general formula (1).

[0154]

(Other additives)

1) Mercapto compounds, disulfides and thiones

In the invention, mercapto compounds, disulfide compounds, and thione compounds may be added in order to control the development by suppressing or enhancing development, to improve spectral sensitization efficiency, or to improve storage properties before and after development. Descriptions can be found in paragraph Nos. 0067 to 0069 of JP-A No. 10-62899, a compound expressed by general formula (I) of JP-A No. 10-186572 and specific examples thereof shown in paragraph Nos. 0033 to 0052, and in lines 36 to 56 in page 20 of EP No. 0803764A1. Among them, mercapto-substituted heterocyclic aromatic compound described in JP-A Nos. 9-297367, 9-304875, and 2001-100358, as well as in Japanese Patent Application Nos. 2001-104213 and 2001-104214, and the like, are particularly preferred.

[0155]

2) Toner

In the photothermographic material of the present invention, the addition of a toner is preferred. The description of the toner can be found in JP-A No.10-62899 (paragraph Nos. 0054 to 0055), EP-A No.0803764A1 (page21, lines 23 to 48), JP-A Nos.2000-356317 and 2000-187298. Particularly preferred are phthalazinones (phthalazinone, phthalazinone derivatives and metal salts thereof, e.g.,4-(1-naphthyl)phthalazinone,6-chlorophthalazinone, 5,7-dimethoxyphthalazinone and 2,3-dihydro-1,4-phthalazinedione); combinations of phthalazinones and phthalic acids(e.g., phthalic acid, 4-methylphthalic acid, 4-nitrophthalic acid, diammonium phthalate, sodium phthalate, potassium phthalate and tetrachlorophthalic anhydride); phthalazines(phthalazine, phthalazine derivatives and metal salts thereof, e.g., 4-(1-naphthyl)phthalazine,6-isopropylphthalazine, 6-tert-butylphthalazine, 6-chlorophthalazine, 5,7-dimethoxyphthalazine and 2,3-dihydrophthalazine). A combination of phthalazines and phthalic acids is preferred, and a combination of phthalazines and phthalic acids is particularly preferred. Particularly preferred among the combinations is a combination of 6-isopropylphthalazine and phthalic acid or 4-methylphthalic acid.

[0156]

The amount of the toner added is 0.01 to 10 mol, preferably 0.05 to 2 mol, per mol of silver coated.

[0157]

As for the tone of output images for medical diagnosis, it is conventionally said that an analyst of X-ray photographs can obtain more precise results of diagnostic observation from output images with cold image tone. Cold image tone herein refers to natural black image tone or blue black image tone. Warm image tone refers to warm brown black image tone.

[0158]

3) Plasticizer and lubricant

Plasticizers and lubricants usable in the photosensitive layer of the invention are described in paragraph No. 0117 of JP-A No. 11-65021. Details on ultra-high contrast promoting agents for forming ultra-high contrast images, and addition amount thereof can be found in paragraph No. 0118, paragraph Nos. 0136 to 0193 of JP-A No. 11-223898, as compounds expressed by formulae (H), (1) to (3), (A), and (B) in JP-A No. 2000-284399, as compounds expressed by formulae (III) to (V) (specific compounds: Formula 21 to Formula 24) in Japanese Patent Application No. 11-91652; as an ultra-high contrast accelerator, description can be found in paragraph No. 0102 of JP-A No. 11-65021, and in paragraph Nos. 0194 to 0195 of JP-A No. 11-223898.

[0159]

4) Dyes and pigments

From the viewpoint of improving image tone, of preventing the generation of interference fringes and of preventing irradiation on laser exposure, various types of dyes and pigments (for instance, C.I. Pigment Blue 60, C.I. Pigment Blue 64, and C.I. Pigment Blue 15:6) may be used in the photosensitive layer of the invention. Detailed description can be found in WO No. 98/36322, JP-A Nos. 10-268465 and 11-338098, and the like.

[0160]

5) Ultra-high contrast promoting agent

In order to form an ultra-high contrast image suitable for use in graphic arts, it is preferred to add an ultra-high contrast promoting agent into the image forming layer. Details on the ultra-high contrast promoting agents, method of their addition and addition amount can be found in paragraph No. 0118, paragraph Nos. 0136 to 0193 of JP-A No. 11-223898, as compounds expressed by formulae (H), (1) to (3), (A), and (B) in Japanese Patent Application No. 11-87297, as compounds expressed by formulae (III) to (V) (specific compounds: Formula 21 to Formula 24) in Japanese Patent Application No. 11-91652; as an ultra-high contrast accelerator, description can be found in paragraph No. 0102 of JP-A No. 11-65021, and in paragraph Nos. 0194 to 0195 of JP-A No. 11-223898.

[0161]

In the case of using formic acid or formates as a strong fogging agent, it is preferably incorporated into the side having thereon the image forming layer containing photosensitive silver halide, in an amount of 5 mmol or less, preferably, one mmol or less per one mol of silver.

[0162]

In the case of using an ultra-high contrast promoting agent in the photothermographic material of the invention, it is preferred to use an acid resulting from hydration of diphosphorus pentoxide, or its salt in combination. Examples of acids resulting from the hydration of diphosphorus pentoxide or salts thereof include metaphosphoric acid (salt), pyrophosphoric acid (salt), orthophosphoric acid (salt), triphosphoric acid (salt), tetraphosphoric acid (salt), hexametaphosphoric acid (salt), and the like. Particularly preferred acids obtainable by the hydration of diphosphorus pentoxide or salts thereof include orthophosphoric acid (salt) and hexametaphosphoric acid (salt). Specifically mentioned as the salts are sodium orthophosphate, sodium dihydrogen orthophosphate, sodium hexametaphosphate, ammonium hexametaphosphate, and the like.

The amount of usage of the acid obtained by hydration of diphosphorus pentoxide or the salt thereof (i.e., the coverage per 1 m² of the photosensitive material) may be set as desired depending on the sensitivity and fogging, but preferred is an amount of 0.1 mg/m² to 500 mg/m², and more preferably, of 0.5 mg/m² to 100 mg/m².

The reducing agent, the hydrogen-bonding compound, the development accelerator and the polyhalogen compound are preferably used as solid dispersions. A preferable method for producing these solid dispersions is described in JP-A No. 2002-55405.

[0163]

(Preparation and coating of of coating solution)

The temperature for preparing the coating solution for use in the image forming layer of the invention is preferably from 30°C to 65 °C, more preferably, from 35°C to less than 60°C, and most preferably, from 35°C to 55°C. Furthermore, the temperature of the coating solution for the image forming layer immediately after adding the polymer latex is preferably maintained in the temperature range of from 30°C to 65 °C.

[0164]

(Layer constitution and constituting components)

One or more image forming layers of the invention are constructed on a support. In the case of constituting the layer by a single layer, it comprises an organic silver salt, photosensitive silver halide, a reducing agent, and a binder, which may further comprise

additional materials as desired, such as a toner, a coating aid, and other auxiliary agents. In the case of constituting the image forming layer from two layers or more, the first image forming layer (in general, a layer placed adjacent to the support) contains an organic silver salt and a photosensitive silver halide, and some of the other components must be incorporated in the second image forming layer or in the both layers. A multicolor photothermographic material may be constituted so as to include combinations of two layers for each of the colors, or may contain all the components in a single layer as described in USP No. 4,708,928. In the case of multicolor photothermographic material, each of the emulsion layers is maintained distinguished from each other by incorporating functional or non-functional barrier layer between each of the photosensitive layers as described in USP No. 4,460,681.

The photothermographic material according to the invention may have a non-photosensitive layer in addition to the image forming layer. The non-photosensitive layers can be classified depending on the layer arrangement into (a) a surface protective layer provided on the image forming layer (on the side farther from the support), (b) an intermediate layer provided among plural image forming layers or between the image forming layer and the protective layer, (c) an undercoat layer provided between the image forming layer and the support, and (d) a back layer provided to the side opposite to the image forming layer.

[0165]

Furthermore, a layer that functions as an optical filter may be provided as (a) or (b) above. An antihalation layer may be provided as (c) or (d) to the photosensitive material.

[0166]

1) Surface protective layer

The photothermographic material of the invention may further comprise a surface protective layer with an object to prevent adhesion of the image forming layer. The surface protective layer may be a single layer, or plural layers.

Description on the surface protective layer may be found in paragraph Nos. 0119 to 0120 of JP-A No. 11-65021 and in JP-A No. 2000-171936.

Preferred as the binder of the surface protective layer of the invention is gelatin, but polyvinyl alcohol (PVA) may be used preferably instead, or in combination. As gelatin, there can be used an inert gelatin (e.g., Nitta gelatin 750), a phthalated gelatin (e.g., Nitta gelatin 801), and the like. Usable as PVA are those described in paragraph Nos. 0009 to 0020 of JP-A No. 2000-171936, and preferred are the completely saponified product PVA-105 and the partially saponified PVA-205 and PVA-335, as well as modified polyvinyl alcohol MP-203 (trade name of products from Kuraray Ltd.). The coverage of polyvinyl alcohol (per 1 m² of support) in the protective layer (per one layer) is preferably in a range of from 0.3 g/m² to 4.0 g/m², and more preferably, from 0.3 g/m² to 2.0 g/m².

[0167]

The coverage of total binder (inclusive of water-soluble polymer and latex polymer) (per 1 m² of support) in the surface protective layer (per one layer) is preferably in a range of from 0.3 g/m² to 5.0 g/m², and more preferably, from 0.3 g/m² to 2.0 g/m².

[0168]

2) Antihalation layer

The photothermographic material of the present invention may comprise an

antihalation layer provided to the side farther from the light source with respect to the photosensitive layer.

[0169]

Descriptions on the antihalation layer can be found in paragraph Nos. 0123 to 0124 of JP-A No. 11-65021, in JP-A Nos. 11-223898, 9-230531, 10-36695, 10-104779, 11-231457, 11-352625, 11-352626, and the like.

The antihalation layer contains an antihalation dye having its absorption at the wavelength of the exposure light. In the case the exposure wavelength is in the infrared region, an infrared-absorbing dye may be used, and in such a case, preferred are dyes having no absorption in the visible region.

In the case of preventing halation from occurring by using a dye having absorption in the visible region, it is preferred that the color of the dye would not substantially reside after image formation, and is preferred to employ a means for bleaching color by the heat of thermal development; in particular, it is preferred to add a thermal bleaching dye and a base precursor to the non-photosensitive layer to impart function as an antihalation layer. Those techniques are described in JP-A No. 11-231457 and the like.

[0170]

The amount of the thermal bleaching dye added is determined depending on the usage of the dye. In general, it is used in such an amount that the optical density (absorbance) exceeds 0.1 when measured at the desired wavelength. The optical density is preferably in a range of from 0.15 to 2, and more preferably, from 0.2 to 1. The usage of dyes to obtain optical density in the above range is generally from about 0.001 g/m² to 1 g/m².

[0171]

By thermal bleaching the dye in such a manner, the optical density after thermal development can be lowered to 0.1 or lower. Two or more types of thermal bleaching dyes may be used in combination in a photothermographic material. Similarly, two or more types of base precursors may be used in combination.

In thermal bleaching process using such a thermal bleaching dye and a base precursor, preferred is to use a substance (for instance, diphenylsulfone, 4-chlorophenyl(phenyl)sulfone, 2-naphthyl benzoate and the like) as disclosed in JP-A No. 11-352626, as well as 2-naphthyl benzoate and the like, which is capable of lowering the melting point of a base precursor by 3°C or more when mixed with a basic precursor from the viewpoint of thermal bleaching property or the like.

[0172]

3) Back layer

Back layers usable in the invention are described in paragraph Nos. 0128 to 0130 of JP-A No. 11-65021.

[0173]

In the invention, coloring matters having maximum absorption in the wavelength range of from 300 nm to 450 nm may be added in order to improve a color tone of developed images and a deterioration of the images during aging. Such coloring matters are described in, for example, JP-A Nos. 62-210458, 63-104046, 63-103235, 63-208846, 63-306436, 63-314535, 01-61745, 2001-100363, and the like.

Such coloring matters are generally added in the range of from 0.1 mg/m² to 1 g/m², preferably to the back layer provided to the side opposite to the photosensitive layer.

In order to control the basic color tone, it is preferred to use a dye having an absorption peak in the wavelength range of from 580 to 680 nm. As a dye satisfying this purpose, preferred are oil-soluble azomethine dyes described in JP-A Nos. 4-359967 and 4-359968, or water-soluble phthalocyanine dyes described in Japanese Patent Application No. 2002-96797, which have low absorption intensity on the short wavelength side. The dyes for this purpose may be added to any of the layers, but more preferred is to add them in the non-photosensitive layer on the emulsion plane side, or in the back plane side.

[0174]

The photothermographic material of the invention is preferably a so-called one-side photosensitive material, which comprises at least one layer of a photosensitive layer containing silver halide emulsion on one side of the support, and a back layer on the other side.

[0175]

4) Matting agent

A matting agent may be preferably added to the photothermographic material of the invention in order to improve transportability. Description on the matting agent can be found in paragraphs Nos. 0126 to 0127 of JP-A No.11-65021. The amount of the matting agents added is preferably in the range from 1 mg/m² to 400 mg/m², more preferably, from 5 mg/m² to 300 mg/m², with respect to the coating amount per one m² of the photosensitive material.

There is no particular restriction on the shape of the matting agent usable in the invention and it may have fixed form or non-fixed form. Preferred is to use those having fixed form and globular shape. Average particle size is preferably in the range of from 0.5 µm to 10 µm, more preferably, from 1.0 µm to 8.0 µm, and most preferably, from 2.0 µm to 6.0 µm. Furthermore, the particle distribution of the matting agent is preferably set such that the variation coefficient may become 50 % or lower, more preferably, 40 % or lower, and most preferably, 30 % or lower. The variation coefficient herein is defined by (the standard deviation of particle diameter)/(mean diameter of the particle) x 100. Furthermore, two types of matting agents having low variation coefficient and the ratio of their mean diameters is more than 3 are preferably blended.

The matness on the emulsion surface is not restricted unless star-dust trouble occurs, but the matness of 30 seconds to 2000 seconds is preferred, and the matness of 40 seconds to 1500 seconds is particularly preferred as Beck's smoothness. Beck's smoothness can be calculated easily, by seeing Japan Industrial Standard (JIS) P8119 "The method of testing Beck's smoothness for papers and sheets using Beck's test apparatus", or TAPPI standard method T479.

[0176]

The matt degree of the back layer in the invention is preferably in a range of 1200 seconds to 10 seconds; more preferably, 800 seconds to 20 seconds, and particularly preferably 500 to 40 seconds, as expressed by Beck smoothness.

[0177]

In the invention, the matting agent is incorporated preferably in the outermost surface layer on the photosensitive layer plane or a layer functioning as the outermost surface layer, or a layer near the outer surface, and a layer that functions as the so-called

protective layer.

[0178]

5) Polymer latex

In the case of the photothermographic material of the invention for graphic arts in which dimensional change is critical, it is preferred to incorporate polymer latex in the surface protective layer and the back layer. As such polymer latexes, descriptions can be found in "Gosei Jushi Emulsion (Synthetic resin emulsion)" (Taira Okuda and Hiroshi Inagaki, Eds., published by Kobunshi Kankokai (1978)), "Gosei Latex no Ouyou (Application of synthetic latex)" (Takaaki Sugimura, Yasuo Kataoka, Soichi Suzuki, and Keiji Kasahara, Eds., published by Kobunshi Kankokai (1993)), and "Gosei Latex no Kagaku (Chemistry of synthetic latex)" (Soichi Muroi, published by Kobunshi Kankokai (1970)). More specifically, there can be mentioned a latex of methyl methacrylate (33.5 % by mass)/ethyl acrylate (50 % by mass)/methacrylic acid (16.5 % by mass) copolymer, a latex of methyl methacrylate (47.5 % by mass)/butadiene (47.5 % by mass)/itaconic acid (5 % by mass) copolymer, a latex of ethyl acrylate/methacrylic acid copolymer, a latex of methyl methacrylate (58.9 % by mass)/2-ethylhexyl methacrylate (25.4 % by mass)/styrene (8.6 % by mass)/2-hydroethyl methacrylate (5.1 % by mass)/acrylic acid copolymer, a latex of methyl methacrylate (64.0 % by mass)/styrene (9.0 % by mass)/butyl acrylate (20.0 % by mass)/2-hydroxyethyl methacrylate(5.0 % by mass)/acrylic acid copolymer, and the like. Furthermore, as the binder for the surface protective layer, there can be applied a combination of polymer latex described in the specification of Japanese Patent Application No. 11-6872, the technology described in paragraph Nos. 0021 to 0025 of the specification of JP-A No. 2000-267226, the technology described in paragraph Nos. 0027 and 0028 of the specification of Japanese Patent Application No. 11-6872, and the technology described in paragraph Nos. 0023 to 0041 of the specification of JP-A No. 2000-19678. The polymer latex in the surface protective layer preferably is contained in an amount of 10 % by mass to 90 % by mass, particularly preferably, of 20 % by mass to 80 % by mass of the total weight of binder.

[0179]

6) Surface pH

The surface pH of the photothermographic material according to the invention is preferably 7.0 or lower, more preferably, 6.6 or lower, before thermal development treatment. Although there is no particular restriction concerning the lower limit, the pH value is about 3, and the most preferred surface pH range is from 4 to 6.2. From the viewpoint of reducing the surface pH, it is preferred to use an organic acid such as phthalic acid derivative or a non-volatile acid such as sulfuric acid, or a volatile base such as ammonia for the adjustment of the surface pH. In particular, ammonia can be used favorably for the achievement of low surface pH, because it can easily vaporize and can be removed before the coating step or before applying thermal development.

It is also preferred to use a non-volatile base such as sodium hydroxide, potassium hydroxide, lithium hydroxide, and the like, in combination with ammonia. The method of measuring a surface pH value is described in paragraph No. 0123 of the specification of JP-A No. 2000-284399.

[0180]

7) Hardener

A hardener can be used in each of image forming layer, protective layer, back layer, and the like. As examples of the hardener, descriptions of various methods can be

found in pages 77 to 87 of T.H. James, "THE THEORY OF THE PHOTOGRAPHIC PROCESS, FOURTH EDITION" (Macmillan Publishing Co., Inc., 1977). Preferably used are, in addition to chromium alum, sodium salt of 2,4-dichloro-6-hydroxy-s-triazine, N,N-ethylene bis(vinylsulfonacetamide), and N,N-propylene bis(vinylsulfonacetamide), polyvalent metal ions described in page 78 of the above literature and the like, polyisocyanates described in USP No. 4,281,060, JP-A No. 6-208193 and the like, epoxy compounds of USP No. 4,791,042 and the like, and vinyl sulfone based compounds of JP-A No. 62-89048.

[0181]

The hardener is added as a solution, and the solution is added to the coating solution for forming the protective layer 180 minutes before coating to just before coating, preferably 60 minutes before to 10 seconds before coating. However, so long as the effect of the invention is sufficiently exhibited, there is no particular restriction concerning the mixing method and the conditions of mixing. As specific mixing methods, there can be mentioned a method of mixing in the tank, in which the average stay time calculated from the flow rate of addition and the feed rate to the coater is controlled to yield a desired time, or a method using static mixer as described in Chapter 8 of N. Harnby, M.F. Edwards, A.W. Nienow (translated by Koji Takahashi) "Liquid Mixing Technology" (Nikkan Kogyo Shinbun, 1989), and the like.

[0182]

8) Surface active agent

As the surface active agent, the solvent, the support, antistatic agent or the electrically conductive layer, and the method for obtaining color images applicable in the invention, there can be mentioned those disclosed in paragraph Nos. 0132, 0133, 0134, 0135, and 0136, respectively, of JP-A No. 11-65021. The lubricant is described in paragraph Nos. 0061 to 0064 of JP-A No. 11-84573 and in paragraph Nos. 0049 to 0062 of Japanese Patent Application No. 11-106881.

In the invention, preferably used is a fluorocarbon surface active agent. Specific examples of fluorocarbon surface active agents can be found in those described in JP-A Nos. 10-197985, 2000-19680, and 2000-214554. Polymer fluorocarbon surface active agents described in JP-A 9-281636 can be also used preferably. For the photothermographic material in the invention, the fluorocarbon surface active agents described in JP-A Nos. 2002-82411, 2001-242357, and 2001-264110 are preferably used. Especially, the use of the fluorocarbon surface active agents described in JP-A Nos. 2001-242357 and 2001-264110 in an aqueous coating solution is preferred from the standpoint of capacity in static control, stability of the coating side state and sliding facility. The fluorocarbon surface active agent described in JP-A No. 2001-264110 is mostly preferred because of high capacity in static control and that it needs small amount to use.

According to the invention, the fluorocarbon surface active agent can be used on either image forming layer side or back layer side, but is preferred to use on the both sides. Further, it is particularly preferred to use the fluorocarbon surface active agent in combination with an electrically conductive layer including aforementioned metal oxides. In this case, the amount of the fluorocarbon surface active agent on the side of the electrically conductive layer can be reduced or removed.

The amount of the fluorocarbon surface active agent used is preferably in the range of 0.1 mg/m² to 100 mg/m² on each side of image forming layer and back layer, more preferably 0.3 mg/m² to 30 mg/m², further preferably 1 mg/m² to 10 mg/m². Especially, the fluorocarbon surface active agent described in JP-A No. 2001-264110 is

effective, and is used preferably in the range of 0.01 mg/m² to 10 mg/m², more preferably 0.01 mg/m² to 5 mg/m².

[0183]

9) Antistatic agent

The photothermographic material of the invention preferably contains an electrically conductive layer including metal oxides or electrically conductive polymers. The antistatic layer may serve as an undercoat layer, or a back surface protective layer, and the like, but can also be placed specially. As an electrically conductive material of the antistatic layer, metal oxides having enhanced electric conductivity by the method of introducing oxygen defects or different types of metallic atoms into the metal oxides are preferably for use. Examples of metal oxides are preferably selected from ZnO, TiO₂ and SnO₂. As the combination of different types of atoms, preferred are ZnO combined with Al, In; SnO₂ with Sb, Nb, P, halogen atoms, and the like; TiO₂ with Nb, Ta, and the like; Particularly preferred for use is SnO₂ combined with Sb. The amount of different types of atoms added is preferably in a range of from 0.01 mol% to 30 mol%, and particularly preferably, in a range of from 0.1 mol% to 10 mol%. The shape of the metal oxides can include, for example, spherical, needle-like, or plate-like shape. The needle-like particles, with the rate of (the major axis)/(the minor axis) is more than two, or more preferably, 3.0 to 50, is preferred from the standpoint of the electric conductivity effect. The metal oxides is used in an amount in the range of preferably from 1 mg/m² to 1000 mg/m², more preferably from 10 mg/m² to 500 mg/m², and further preferably from 20 mg/m² to 200 mg/m². The antistatic layer can be laid on either side of the emulsion side or the back layer side, it is preferred to set between the support and the back layer. Examples of the antistatic layer in the invention are described in JP-A Nos. 11-65021, 56-143430, 56-143431, 58-62646, and 56-120519, and in paragraph Nos. 0040 to 0051 of JP-A No. 11-84573, US-P No. 5575957, and in paragraph Nos. 0078 to 0084 of JP-A No. 11-223898.

[0184]

10) Support

As the transparent support, favorably used is polyester, particularly, polyethylene terephthalate, which is subjected to heat treatment in the temperature range of from 130°C to 185°C in order to relax the internal strain caused by biaxial stretching and remaining inside the film, and to remove strain ascribed to heat shrinkage generated during thermal development. In the case of a photothermographic material for medical use, the transparent support may be colored with a blue dye (for instance, dye-1 described in the example of JP-A No. 8-240877), or may be uncolored. As to the support, it is preferred to apply undercoating technology, such as water-soluble polyester described in JP-A No. 11-84574, a styrene-butadiene copolymer described in JP-A No. 10-186565, a vinylidene chloride copolymer described in JP-A No. 2000-39684 and in paragraph Nos. 0063 to 0080 of Japanese Patent Application No. 11-106881, and the like.

[0185]

11) Other additives

Furthermore, antioxidant, stabilizing agent, plasticizer, UV absorbent, or a coating aid may be added to the photothermographic material. Each of the additives is added to either the photosensitive layer or the non-photosensitive layer. Reference can be made to WO No. 98/36322, EP-A No. 803764A1, JP-A Nos. 10-186567 and 10-18568, and the like.

[0186]

12) Coating method

The photothermographic material of the invention may be coated by any method. More specifically, various types of coating operations inclusive of extrusion coating, slide coating, curtain coating, immersion coating, knife coating, flow coating, or an extrusion coating using the type of hopper described in USP No. 2,681,294 are used. Preferably used is extrusion coating or slide coating described in pages 399 to 536 of Stephen F. Kistler and Peter M. Schweizer, "LIQUID FILM COATING" (Chapman & Hall, 1997), and most preferably used is slide coating. Example of the shape of the slide coater for use in slide coating is shown in Figure 11b.1, page 427, of the same literature. If desired, two or more layers can be coated simultaneously by the method described in pages 399 to 536 of the same literature, or by the method described in USP No. 2,761,791 and British Patent No. 837,095. Particularly preferred in the invention is the method described in JP-A Nos. 2001-194748, 2002-153808, 2002-153803, and 2002-182333.

[0187]

The coating solution for the layer containing organic silver salt in the invention is preferably a so-called thixotropic fluid. For the details of this technology, reference can be made to JP-A No. 11-52509. The viscosity of the coating solution for the layer containing organic silver salt in the invention at a shear velocity of 0.1S^{-1} is preferably from 400 mPa·s to 100,000 mPa·s, and more preferably, from 500 mPa·s to 20,000 mPa·s. At a shear velocity of 1000S^{-1} , the viscosity is preferably from 1 mPa·s to 200 mPa·s, and more preferably, from 5 mPa·s to 80 mPa·s.

[0188]

In the case of mixing two types of liquids in preparing the coating solution of the invention, known in-line mixer and in-plant mixer can be used favorably. Preferred in-line mixer of the invention is described in JP-A No. 2002-85948, and the in-plant mixer is described in JP-A No. 2002-90940.

The coating solution of the invention is preferably subjected to defoaming treatment to maintain the coated surface in a fine state. Preferred defoaming treatment method in the invention is described in JP-A No. 2002-66431.

In the case of applying the coating solution of the invention to the support, it is preferred to perform diselectrification in order to prevent the adhesion of dust, particulates, and the like due to charge up. Preferred example of the method of diselectrification for use in the invention is described in JP-A No. 2002-143747.

Since a non-setting coating solution is used for the image forming layer in the invention, it is important to precisely control the drying wind and the drying temperature. Preferred drying method for use in the invention is described in detail in JP-A Nos. 2001-194749 and 2002-139814.

In order to improve the film-forming properties in the photothermographic material of the invention, it is preferred to apply a heat treatment immediately after coating and drying. The temperature of the heat treatment is preferably in a range of from 60 °C to 100°C at the film surface, and heating time is preferably in a range of from 1 second to 60 seconds. More preferably, heating is performed in a temperature range of from 70 °C to 90 °C at the film surface for a duration of from 2 seconds to 10 seconds. A preferred method of heat treatment for the invention is described in JP-A No. 2002-107872.

Furthermore, the production methods described in JP-A Nos. 2002-156728 and 2002-182333 are favorably used in the invention in order to stably and continuously produce the photothermographic material of the invention.

[0189]

The photothermographic material is preferably of mono-sheet type (i.e., a type which can form image on the photothermographic material without using other sheets such as an image-receiving material).

[0190]

13) Wrapping material

In order to suppress fluctuation from occurring on the photographic performance during preservation of the photosensitive material of the invention before thermal development, or in order to improve curling or winding tendencies, it is preferred that the photothermographic material is sealed by a wrapping material having low oxygen transmittance and/or vapor transmittance. Preferably, oxygen transmittance is 50 ml/atm·m²·day or lower at 25°C, more preferably, 10 ml/atm·m²·day or lower, and most preferably, 1.0 ml/atm·m²·day or lower. Preferably, vapor transmittance is 10 g/atm·m²·day or lower, more preferably, 5 g/atm·m²·day or lower, and most preferably, 1 g /atm·m²·day or lower.

As specific examples of a wrapping material having low oxygen transmittance and/or vapor transmittance, reference can be made to, for instance, the wrapping material described in JP-A Nos. 8-254793 and 2000-206653.

[0191]

14) Other applicable techniques

Techniques which can be used for the photothermographic material of the invention also include those in EP803764A1, EP883022A1, WO98/36322, JP-A Nos. 56-62648, 58-62644, JP-A Nos. 09-43766, 09-281637, 09-297367, 09-304869, 09-311405, 09-329865, 10-10669, 10-62899, 10-69023, 10-186568, 10-90823, 10-171063, 10-186565, 10-186567, 10-186569 to 10-186572, 10-197974, 10-197982, 10-197983, 10-197985 to 10-197987, 10-207001, 10-207004, 10-221807, 10-282601, 10-288823, 10-288824, 10-307365, 10-312038, 10-339934, 11-7100, 11-15105, 11-24200, 11-24201, 11-30832, 11-84574, 11-65021, 11-109547, 11-125880, 11-129629, 11-133536 to 11-133539, 11-133542, 11-133543, 11-223898, 11-352627, 11-305377, 11-305378, 11-305384, 11-305380, 11-316435, 11-327076, 11-338096, 11-338098, 11-338099, 11-343420, JP-A Nos. 2000-187298, 2000-10229, 2000-47345, 2000-206642, 2000-98530, 2000-98531, 2000-112059, 2000-112060, 2000-112104, 2000-112064 and 2000-171936.

[0192]

In instances of multi-color photothermographic materials, each photosensitive layer is in general held distinctively from each other by using a functional or nonfunctional barrier layer between each photosensitive layer as described in USP No. 4,460,681.

The multi-color photothermographic material may be constituted so as to include a combination of these two layers for each color. Alternatively, all ingredients may be included into a single layer as described in USP No. 4,708,928.

[0193]

(Image forming method)

1) Exposure

Laser used is He-Ne laser of red through infrared emission, red semiconductor laser, or Ar⁺, He-Ne, He-Cd laser of blue through green emission, blue semiconductor laser. More preferable is semiconductor laser of red through infrared emission. The

peak wavelength of the laser light is 600 to 900 nm, and preferably 620 to 850 nm. Meanwhile, modules having SHG (Second Harmonic Generator) chip and semiconductor laser which are integrated, or blue semiconductor laser have been especially developed recently, and thus laser output devices for short wavelength region have attracted the attention. Blue semiconductor laser has been expected as a light source with increasing demand hereafter because image recording with high definition is possible, and increased recording density, as well as stable output with longer operating life are enabled. The peak wavelength of the blue laser light is 300 to 500 nm, and preferably 400 to 500 nm.

Laser beam which oscillates in a longitudinal multiple modulation by a method such as high frequency superposition is also preferably employed.

[0194]

2) Thermal development

The temperature for the development is preferably 80°C to 250°C, preferably 100°C to 140°C, and more preferably 110°C to 130°C. Time period for the development is preferably 1 second to 60 seconds, more preferably 3 seconds to 30 seconds, particularly preferably 5 seconds to 25 seconds, and most preferably 7 seconds to 15 seconds.

[0195]

In the process for the thermal development, either drum type heaters or plate type heaters may be used. However, plate type heater processes are more preferred. Preferable process for the thermal development by a plate type heater may be a process described in JP-A No. 11-133572, which discloses a thermal developing device in which a visible image is obtained by bringing a photothermographic material with a latent image into contact with a heating means at a thermal development region, wherein the heating means comprises a plate heater, and a plurality of retainer rollers are oppositely provided along one surface of the plate heater, the thermal developing device being characterized in that thermal development is performed by passing the photothermographic material between the retainer rollers and the plate heater. It is preferred that the plate heater is divided into 2 to 6 sections, with the leading end having a temperature lowered by 1 to 10°C. For example, 4 sets of plate heaters which can be independently subjected to the temperature control are used, and are controlled so that they respectively become 112°C, 119°C, 121°C, and 120°C. Such a process is also described in JP-A No. 54-30032, which allows for excluding moisture and organic solvents included in the photothermographic material out of the system, and also allows for suppressing the change of shapes of the support of the photothermographic material upon rapid heating of the photothermographic material.

[0196]

It is preferable to control a heater more stably to reduce the size of the thermal developing device and reduce time for thermal development. It is also preferable to begin thermal development when a sheet of photosensitive material is in a state in which the leading end, which has been exposed, begins to be thermal developed while the trailing end is still unexposed. An example of an imager that provides rapid processing preferable in the present invention is described in, for example, Japanese Patent Application Nos. 2001-088832, 2001-091114, 2001-170642 and 2002-92635. The imager disclosed in these patent applications enables thermal development in 14 seconds in a three-staged plate heater of which temperature is controlled to, for example, 107°C-121°C-121°C. The time before the first sheet is outputted is reduced to about 60 seconds.

[0197]

The present invention is an image forming method using a photothermographic material, wherein the photothermographic material is discharged from a thermal developing device within 35 seconds after heating for thermal development is ceased. When the photothermographic material is heated by a three plate-type heater, "after heating for thermal development" refers to the time when the photosensitive material is conveyed away from the last third plate. This time may be different for a leading end and a trailing end of the same sheet of photosensitive material conveyed. In such a case, this time refers to the time when each part of the photosensitive material is conveyed away from the plate. Namely, the time at which "heating for thermal development is ceased" varies for each part of the photosensitive material.

"Discharged from a thermal developing device" means that the photosensitive material is taken out from the thermal developing device on completion of the thermal development. The photosensitive material is exposed to light when taken out from the thermal developing device. In a developing device, the photosensitive material is generally conveyed from the developing section and discharged automatically. The photosensitive material is regarded as having been discharged when it is accommodated in a tray. The image forming method of the invention is applied to the case in which the photosensitive material in the developing device is taken out by hand, so long as the time between when the photosensitive material is conveyed away from the heating section and when the photosensitive material is taken out from the thermal development device is 35 seconds or less.

"X" in Fig. 1 refers to the time when heating is ceased, and "Y" refers to the time when the photosensitive material is discharged from between discharging rollers 63. The time between X and Y is 35 seconds or less. Stable output images can be obtained by using the photothermographic material of the invention.

[0198]

3) System

Examples of a medical laser imager equipped with a light exposing part and a thermal developing part include Fuji Medical Dry Laser Imager FM-DP L. In connection with the FM-DPL, description is found in Fuji Medical Review No. 8, pages 39-55. It goes without mentioning that those techniques may be applied as the laser imager for the photothermographic material of the invention. In addition, the present photothermographic material can be also applied as a photothermographic material for the laser imager used in "AD network" which was proposed by Fuji Film Medical Co., Ltd. as a network system accommodated to DICOM standard.

[0199]

(Application of the invention)

The image forming method in which the photothermographic material of the invention is used is preferably employed as an image forming method for photothermographic materials for use in medical imaging, photothermographic materials for use in industrial photographs, photothermographic materials for use in graphic arts, as well as for COM, through forming black and white images by silver imaging.

[0200]

[Examples]

The present invention is specifically explained by way of Examples below, which should not be construed as limiting the invention thereto.

[0201]

Example 1

(Preparation of PET Support)

1) Film Manufacturing

PET having IV (intrinsic viscosity) of 0.66 (measured in phenol/tetrachloroethane = 6/4 (weight ratio) at 25°C) was obtained according to a conventional manner using terephthalic acid and ethylene glycol. The product was pelletized, dried at 130°C for 4 hours and melted at 300°C. Thereafter, the mixture was extruded from a T-die and rapidly cooled to form a non-tentered film having such a thickness that the thickness should become 175 µm after tentered and thermal fixation.

[0202]

The film was stretched along the longitudinal direction by 3.3 times using rollers of different peripheral speeds, and then stretched along the transverse direction by 4.5 times using a tenter machine. The temperatures used for these operations were 110°C and 130°C, respectively. Then, the film was subjected to thermal fixation at 240°C for 20 seconds, and relaxed by 4% along the transverse direction at the same temperature. Thereafter, the chucking part was slit off, and both edges of the film were knurled. Then the film was rolled up at the tension of 4 kg/cm² to obtain a roll having the thickness of 175 µm.

[0203]

2) Surface Corona Discharge Treatment

Both surfaces of the support were treated at room temperature at 20 m/minute using Solid State Corona Discharge Treatment Machine Model 6KVA manufactured by Piller GmbH. It was proven that treatment of $0.375 \text{ kV} \cdot \text{A-minute/m}^2$ was executed, judging from the readings of current and voltage on that occasion. The frequency upon this treatment was 9.6 kHz, and the gap clearance between the electrode and dielectric roll was 1.6 mm.

[0204]

3) Undercoating

1) Preparation of Coating Solution for Undercoat Layer

Formula (1) (for undercoat layer on the image forming layer side)

Pesresin A-520 manufactured by Takamatsu Oil & Fat Co., Ltd. (30% by mass solution) 59 g

Polyethyleneglycol monononylphenylether (average ethylene oxide

number = 8.5) 10% by mass solution 5.4 g

MP-1000 manufactured by Soken Chemical & Engineering Co., Ltd. (polymer fine particle, mean particle diameter of 0.4 μm)

0.91 g

Distilled water 935 mL

[0205]

Formula (2) (for first layer on the back surface)

Styrene-butadiene copolymer latex (solid content of 40% by mass, styrene/butadiene weight ratio = 68/32) 158 g

1% by mass aqueous solution of sodium laurylbenzenesulfonate

10 mL

Distilled water

854 mL

[0206]

Formula (3) (for second layer on the back surface)

SnO₂/SbO (9/1 mass ratio, mean particle diameter of 0.038 μm, 17% by mass dispersion)

84 g

Gelatin (10% by mass aqueous solution)

89.2 g

METOLOSE TC-5 manufactured by Shin-Etsu Chemical Co., Ltd. (2% by mass aqueous solution)

8.6 g

MP-1000 manufactured by Soken Chemical & Engineering Co., Ltd.

0.01 g

1% by mass aqueous solution of sodium dodecylbenzenesulfonate

10 mL

NaOH (1% by mass)

6 mL

Proxel (manufactured by Imperial Chemical Industries PLC)

1 mL

Distilled water

805 mL

[0207]

2. Undercoating

Both surfaces of the biaxially tentered polyethylene terephthalate support having the thickness of 175 μm were subjected to the corona discharge treatment as described above. Thereafter, the aforementioned formula (1) of the coating solution for the undercoat was coated on one surface (image forming layer side) with a wire bar so that the amount of wet coating became 6.6 mL/m² (per one side), and dried at 180°C for 5 minutes. Then, the aforementioned formula (2) of the coating solution for the undercoat was coated on the reverse face (back surface) with a wire bar so that the amount of wet coating became 5.7 mL/m², and dried at 180°C for 5 minutes. Furthermore, the aforementioned formula (3) of the coating solution for the undercoat was coated on the reverse face (back surface) with a wire bar so that the amount of wet coating became 7.7 mL/m², and dried at 180°C for 6 minutes. Thus, an undercoated support was produced.

[0208]

(Back layer)

1) Preparation of Coating Solution for Back Layer

(Preparation of Dispersion of Solid Fine Particles (a) of Base Precursor)

A base precursor compound-1 in an amount of 2.5 kg, and 300 g of a surfactant (trade name: DEMOL N, manufactured by Kao Corporation), 800 g of diphenyl sulfone, 1.0 g of benzoisothiazolinone sodium salt and distilled water were added to give the total amount of 8.0 kg and mixed. The mixed liquid was subjected to beads dispersion using a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.). Process for dispersion included feeding the mixed liquid to UVM-2 packed with zirconia beads having the mean particle diameter of 0.5 mm with a diaphragm pump, followed by the dispersion at the inner pressure of 50 hPa or higher until desired mean particle diameter could be achieved.

The dispersion was continued until the ratio of the optical density at 450 nm and the optical density at 650 nm for the spectral absorption of the dispersion (D450/ D650)

became 3.0 upon spectral absorption measurement. Thus resulting dispersion was diluted with distilled water so that the concentration of the base precursor became 25% by weight, filtrated (with a polypropylene filter having the mean fine pore diameter of 3 µm) for eliminating dust, and was put into practical use.

[0209]

2) Preparation of Dispersion of Solid Fine Particle of Dye

A cyanine dye compound-1 in an amount of 6.0 kg, and 3.0 kg of sodium p-dodecylbenzenesulfonate, 0.6 kg of DEMOL SNB (a surfactant manufactured by Kao Corporation), and 0.15 kg of a defoaming agent (trade name: SURFYNOL 104E, manufactured by Nissin Chemical Industry Co., Ltd.) were mixed with distilled water to give the total liquid amount of 60 kg. The mixed liquid was subjected to dispersion with 0.5 mm zirconia beads using a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.).

The dispersion was dispersed until the ratio of the optical density at 650 nm and the optical density at 750 nm for the spectral absorption of the dispersion (D650/ D750) became 5.0 or greater upon spectral absorption measurement. Thus resulting dispersion was diluted with distilled water so that the concentration of the cyanine dye became 6% by mass, filtrated with a filter (mean fine pore diameter: 1 µm) for eliminating dust, and was put into practical use.

[0210]

3) Preparation of Coating Solution for Antihalation Layer

A vessel was kept at 40°C, and thereto were added 40 g of gelatin, 20 g of monodispersed polymethyl methacrylate fine particles (mean particle size of 8 µm, standard deviation of particle diameter of 0.4), 0.1 g of benzoisothiazolinone and 490 mL of water to allow gelatin to be dissolved. Additionally, 2.3 mL of a 1 mol/L aqueous sodium hydroxide solution, 40 g of the aforementioned dispersion of the solid fine particle of the dye, 90 g of the aforementioned dispersion of the solid fine particles (a) of the base precursor, 12 mL of a 3% by weight aqueous solution of sodium polystyrenesulfonate, and 180 g of a 10% by weight solution of SBR latex were admixed. Just prior to the coating, 80 mL of a 4% by weight aqueous solution of N,N-ethylenebis(vinylsulfone acetamide) was admixed to give a coating solution for the antihalation layer.

[0211]

4) Preparation of Coating Solution for Back Surface Protective Layer

A vessel was kept at 40°C, and thereto were added 40 g of gelatin, 35 mg of benzoisothiazolinone and 840 ml of water to allow gelatin to be dissolved. Additionally, 5.8 ml of a 1 mol/L aqueous sodium hydroxide solution, liquid paraffin emulsion at 1.5 g equivalent to liquid paraffin, 10 mL of a 5% by weight aqueous solution of di(2-ethylhexyl) sodium sulfosuccinate, 20 mL of a 3% by weight aqueous solution of sodium polystyrenesulfonate, 2.4 mL of a 2% by weight solution of a fluorocarbon surfactant (F-1), 2.4 mL of a 2% by weight solution of a fluorocarbon surfactant (F-2), and 32 g of a 19% by mass solution of methyl methacrylate/ styrene/ butyl acrylate/ hydroxyethyl methacrylate/ acrylic acid copolymer (copolymer weight ratio of 57/8/28/5/2) latex were admixed. Just prior to the coating, 25 mL of a 4% by weight aqueous solution of N,N-ethylenebis(vinylsulfone acetamide) was admixed to give a coating solution for the back surface protective layer.

[0212]

5) Coating of Back Layer

The back surface side of the undercoated support as described above was subjected to simultaneous double coating so that the coating solution for the antihalation layer gives the coating amount of gelatin of 0.52 g/m², and so that the coating solution for the back surface protective layer gives the coating amount of gelatin of 1.7 g/m², followed by drying to produce a back layer.

[0213]

(Image Forming Layer, Intermediate Layer, and Surface Protective Layer)

1. Preparation of Materials for Coating

1) Silver Halide Emulsion

<<Preparation of Silver Halide Emulsion-1>>

To 1421 mL of distilled water was added 3.1 mL of a 1% by mass potassium bromide solution. Further, a liquid added with 3.5 mL of sulfuric acid having the concentration of 0.5 mol/L and 31.7 g of phthalated gelatin was kept at 30°C while stirring in a stainless steel reaction pot, and thereto were added total amount of: solution A prepared through diluting 22.22 g of silver nitrate by adding distilled water to give the volume of 95.4 mL; and solution B prepared through diluting 15.3 g of potassium bromide and 0.8 g of potassium iodide with distilled water to give the volume of 97.4 mL, over 45 seconds at a constant flow rate. Thereafter, 10 mL of a 3.5% by mass aqueous solution of hydrogen peroxide was added thereto, and 10.8 mL of a 10% by mass aqueous solution of benzimidazole was further added. Moreover, a solution C prepared through diluting 51.86 g of silver nitrate by adding distilled water to give the volume of 317.5 mL and a solution D prepared through diluting 44.2 g of potassium bromide and 2.2 g of potassium iodide with distilled water to give the volume of 400 mL were added. A controlled double jet method was executed through adding total amount of the solution C at a constant flow rate over 20 minutes, accompanied by adding the solution D while maintaining the pAg at 8.1. Hexachloroiridium (III) potassium salt was added to give 1 x 10⁻⁴ mol per one mol of silver at 10 minutes post initiation of the addition of the solution C and the solution D in its entirety. Moreover, at 5 seconds after completing the addition of the solution C, a potassium iron (II) hexacyanide aqueous solution was added at a total amount of 3 x 10⁻⁴ mol per one mol of silver. The mixture was adjusted to the pH of 3.8 with sulfuric acid at the concentration of 0.5 mol/L. After stopping stirring, the mixture was subjected to precipitation/ desalting/ water washing steps. The mixture was adjusted to the pH of 5.9 with sodium hydroxide at the concentration of one mol/L to produce a silver halide dispersion having the pAg of 8.0.

[0214]

The silver halide dispersion was kept at 38°C with stirring, and thereto was added 5 mL of a 0.34% by mass methanol solution of 1,2-benzoisothiazoline-3-one, followed by elevating the temperature to 47°C at 40 minutes thereafter. 20 minutes after elevating the temperature, sodium benzene thiosulfonate in a methanol solution was added in an amount of 7.6 x 10⁻⁵ mol per one mol of silver. Additional 5 minutes later, a tellurium sensitizer C in a methanol solution was added in an amount of 2.9 x 10⁻⁴ mol per one mol of silver and subjected to aging for 91 minutes. Thereafter, a methanol solution of a spectral sensitizer A and a spectral sensitizer B with a molar ratio of 3 : 1 was added thereto in an amount of 1.2 x 10⁻³ mol in total of the spectral sensitizer A and B per one mol of silver. One minute later, 1.3 mL of a 0.8% by mass N,N'-dihydroxy-N'',N''-diethylmelamine in methanol was added thereto, and additional 4 minutes thereafter, 5-methyl-2-mercaptobenzimidazole in a methanol solution in an amount of 4.8 x 10⁻³ mol per one mol

of silver, 1-phenyl-2-heptyl-5-mercaptop-1,3,4-triazole in a methanol solution in an amount of 5.4×10^{-3} mol per one mol of silver, and 1-(3-methylureidophenyl)-5-mercaptotetrazole in an aqueous solution in an amount of 8.5×10^{-3} mol per one mol of silver were added to produce a silver halide emulsion-1.

[0215]

Grains in thus prepared silver halide emulsion were silver iodide bromide grains having a mean sphere equivalent diameter of $0.042 \mu\text{m}$, a variation coefficient of 20%, which uniformly include iodine in an amount of 3.5 mol%. Grain size and the like were determined from the average of 1000 grains using an electron microscope. The [100] face ratio of these grains were found to be 80% using a Kubelka-Munk method.

[0216]

<<Preparation of Silver Halide Emulsion-2>>

Preparation of silver halide emulsion-2 was conducted in a similar manner to the process in the preparation of the silver halide emulsion-1 except that: the temperature of the liquid upon the nucleation process was altered from 30°C to 47°C ; the solution B was changed to that prepared by diluting 15.9 g of potassium bromide with distilled water to give the volume of 97.4 mL; the solution D was changed to that prepared by diluting 45.8 g of potassium bromide with distilled water to give the volume of 400 mL; time period for adding the solution C was changed to 30 minutes; and potassium iron (II) hexacyanide was deleted. The precipitation/ desalting/ water washing /dispersion were carried out similarly to the silver halide emulsion-1. Furthermore, the spectral sensitization, chemical sensitization, and addition of 5-methyl-2-mercaptopbenzimidazole and 1-phenyl-2-heptyl-5-mercaptop-1,3,4-triazole was executed similarly to the emulsion-1 except that: the amount of the tellurium sensitizer C to be added was changed to 1.1×10^{-4} mol per one mol of silver; the amount of the methanol solution of the spectral sensitizer A and a spectral sensitizer B with a molar ratio of 3 : 1 to be added was changed to 7.0×10^{-4} mol in total of the spectral sensitizer A and the spectral sensitizer B per one mol of silver; the addition of 1-phenyl-2-heptyl-5-mercaptop-1,3,4-triazole was changed to give 3.3×10^{-3} mol per one mol of silver; and the addition of 1-(3-methylureidophenyl)-5-mercaptotetrazole was changed to give 4.7×10^{-3} mol per one mol of silver to produce a silver halide emulsion-2. The emulsion grains in the silver halide emulsion-2 were pure cubic silver bromide grains having a mean sphere equivalent diameter of $0.080 \mu\text{m}$ and a variation coefficient of 20%.

[0217]

<<Preparation of Silver Halide Emulsion-3>>

Preparation of a silver halide emulsion-3 was conducted in a similar manner to the process in the preparation of the silver halide emulsion-1 except that the temperature of the liquid upon the nucleation process was altered from 30°C to 27°C . In addition, the precipitation/ desalting/ water washing /dispersion were carried out similarly to the silver halide emulsion-1. Silver halide emulsion-3 was obtained similarly to the emulsion-1 except that: the addition of the methanol solution of the spectral sensitizer A and the spectral sensitizer B was changed to the solid dispersion (aqueous gelatin solution) at a molar ratio of 1 : 1 with the amount to be added being 6.0×10^{-3} mol in total of the spectral sensitizer A and spectral sensitizer B per one mol of silver; the amount of the tellurium sensitizer C to be added was changed to 5.2×10^{-4} mol per one mol of silver; and bromoauric acid at 5×10^{-4} mol per one mol of silver and potassium thiocyanate at 2×10^{-3} mol per one mol of silver were added 3 minutes after the addition of the tellurium

sensitizer. The grains in the silver halide emulsion-3 were silver iodide bromide grains having a mean sphere equivalent diameter of 0.034 µm and a variation coefficient of 20%, which uniformly include iodine at 3.5 mol%.

[0218]

<<Preparation of Mixed Emulsion A for Coating Solution>>

The silver halide emulsion-1 in an amount of 70% by mass, the silver halide emulsion-2 in an amount of 15% by mass and the silver halide emulsion-3 in an amount of 15% by mass were dissolved, and thereto was added benzothiazolium iodide in an amount of 7×10^{-3} mol per one mol of silver with a 1% by mass aqueous solution. Further, water was added thereto to give the content of silver of 38.2 g per one kg of the mixed emulsion for a coating solution, and 1-(3-methylureidophenyl)-5-mercaptotetrazole was added to give 0.34 g per 1 kg of the mixed emulsion for a coating solution.

[0219]

2) Preparation of Dispersion of Silver Salt of Fatty Acid

[0220]

<<Preparation of Dispersion of Silver Salt of Fatty Acid 1>>

87.6 kg of behenic acid (Henkel Co., trade name: Edenor C22-85R), 423 L of distilled water, 49.2 L of an aqueous NaOH solution at the concentration of 5 mol/L, 120 L of t-butyl alcohol were admixed, and subjected to a reaction with stirring at 75°C for one hour to give a solution A of sodium behenate. Separately, 206.2 L of an aqueous solution of 40.4 kg of silver nitrate (pH 4.0) was provided, and kept at a temperature of 10°C. A reaction vessel charged with 635 L of distilled water and 30 L of t-butyl alcohol was kept at 30°C, and thereto were added the total amount of the solution A of sodium behenate and the total amount of the aqueous silver nitrate solution with sufficient stirring at a constant flow rate over 93 minutes and 15 seconds, and 90 minutes, respectively. Upon this operation, during first 11 minutes following the initiation of adding the aqueous silver nitrate solution, the added material was restricted to the aqueous silver nitrate solution alone. The addition of the solution A of sodium behenate was thereafter started, and during 14 minutes and 15 seconds following the completion of adding the aqueous silver nitrate solution, the added material was restricted to the solution A of sodium behenate alone. The temperature inside of the reaction vessel was then set to be 30°C, and the temperature outside was controlled so that the liquid temperature could be kept constant. In addition, the temperature of a pipeline for the addition system of the solution A of sodium behenate was kept constant by circulation of warm water outside of a double wall pipe, so that the temperature of the liquid at an outlet in the leading edge of the nozzle for addition was adjusted to be 75°C. Further, the temperature of a pipeline for the addition system of the aqueous silver nitrate solution was kept constant by circulation of cool water outside of a double wall pipe. Position at which the solution A of sodium behenate was added and the position at which the aqueous silver nitrate solution was added were arranged symmetrically with a shaft for stirring located at a center. Moreover, both of the positions were adjusted to avoid contact with the reaction liquid.

[0221]

After completing the addition of the solution A of sodium behenate, the mixture was left to stand at the temperature as it was for 20 minutes. The temperature of the mixture was then elevated to 35°C over 30 minutes followed by aging for 210 minutes. Immediately after completing the aging, solid matters were filtered out with centrifugal

filtration. The solid matters were washed with water until the electric conductivity of the filtrated water became 30 $\mu\text{S}/\text{cm}$. A silver salt of the fatty acids was thus obtained. The resulting solid matters were stored as a wet cake without drying.

[0222]

When the shape of the resulting particles of the silver behenate was evaluated by an electron micrography, it was revealed that a flake crystal had the following: $a = 0.14 \mu\text{m}$, $b = 0.4 \mu\text{m}$ and $c = 0.6 \mu\text{m}$ on the average value, a mean aspect ratio of 5.2, an average equivalent particle size of 0.52 μm and a variation coefficient of 11% (a , b and c are as defined aforementioned).

[0223]

To the wet cake corresponding to 260 kg of a dry solid matter content, were added 19.3 kg of polyvinyl alcohol (trade name: PVA-217) and water to give the total amount of 1000 kg. Then, slurry was obtained from the mixture using a dissolver blade. Additionally, the slurry was subjected to preliminary dispersion with a pipeline mixer (manufactured by MIZUHO Industrial Co., Ltd.: PM-10 type).

[0224]

Next, a stock liquid after the preliminary dispersion was treated three times using a dispersing machine (trade name: Microfluidizer M-610, manufactured by Microfluidex International Corporation, using Z type Interaction Chamber) with the pressure controlled to be 1260 kg/cm^2 to give a dispersion 1 of the silver salt of fatty acid. For the cooling manipulation, coiled heat exchangers were provided at the front and the rear of the interaction chamber, and accordingly, the temperature for the dispersion was set to be 18°C by regulating the temperature of the cooling medium.

[0225]

3) Preparation of Reducing Agent-1 Dispersion

To 10 kg of a reducing agent-2 (6,6'-di-t-butyl-4,4'-dimethyl-2,2'-butylenediphenol) and 16 kg of a 10% by mass aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP203) was added 10 kg of water, and thoroughly mixed to give slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.) packed with zirconia beads having the mean particle diameter of 0.5 mm for 3 hours and 30 minutes. Thereafter, 0.2 g of a benzoisothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the reducing agent to be 25% by mass. This dispersion was warmed at 40°C for one hour, followed by a subsequent thermal treatment at 80°C for one hour to obtain a reducing agent-2 dispersion. Particles of the reducing agent included in thus resulting reducing agent dispersion had a median diameter of 0.50 μm , and a maximum particle diameter of 1.6 μm or less. The resultant reducing agent dispersion was subjected to filtration with a polypropylene filter having a pore size of 3.0 μm to remove foreign substances such as dust, and was stored.

[0226]

4) Preparation of Hydrogen Bonding Compound-1 Dispersion

To 10 kg of a hydrogen bonding compound-1 (tri(4-t-butylphenyl)phosphineoxide) and 16 kg of a 10% by mass aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP203) was added 10 kg of water, and thoroughly mixed to give slurry. This slurry was fed with a diaphragm pump,

and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.) packed with zirconia beads having the mean particle diameter of 0.5 mm for 4 hours. Thereafter, 0.2 g of a benzoisothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the hydrogen bonding compound to be 25% by mass. This dispersion was warmed at 40°C for one hour, followed by a subsequent thermal treatment at 80°C for one hour to obtain a hydrogen bonding compound-1 dispersion. Particles of the hydrogen bonding compound included in thus resulting hydrogen bonding compound dispersion had a median diameter of 0.45 µm, and a maximum particle diameter of 1.3 µm or less. The resultant hydrogen bonding compound dispersion was subjected to filtration with a polypropylene filter having a pore size of 3.0 µm to remove foreign substances such as dust, and was stored.

[0227]

5) Preparation of Development Accelerator-1 Dispersion

To 10 kg of a development accelerator-1 and 20 kg of a 10% by mass aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP203) was added 10 kg of water, and thoroughly mixed to give slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.) packed with zirconia beads having the mean particle diameter of 0.5 mm for 3 hours and 30 minutes. Thereafter, 0.2 g of a benzoisothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the development accelerating agent to be 20% by mass. Accordingly, a development accelerator-1 dispersion was obtained. Particles of the development accelerator included in thus resulting development accelerator dispersion had a median diameter of 0.48 µm, and a maximum particle diameter of 1.4 µm or less. The resultant development accelerator dispersion was subjected to filtration with a polypropylene filter having a pore size of 3.0 µm to remove foreign substances such as dust, and was stored.

Also concerning solid dispersions of a development accelerator-2 and a color-tone-adjusting agent-1, dispersion was executed in a similar manner to that of the development accelerator-1, and thus dispersions of 20% by mass and 15% by mass were respectively obtained.

[0228]

6) Preparation of Polyhalogen Compound

<<Preparation of Organic Polyhalogen Compound-1 Dispersion>>

An organic polyhalogen compound-1 (tribromomethane sulfonylbenzene) in an amount of 10 kg, 10 kg of a 20% by mass aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP203), 0.4 kg of a 20% by mass aqueous solution of sodium triisopropylnaphthalenesulfonate and 14 kg of water were added, and thoroughly admixed to give slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.) packed with zirconia beads having the mean particle diameter of 0.5 mm for 5 hours. Thereafter, 0.2 g of a benzoisothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the organic polyhalogen compound to be 26% by mass. Accordingly, an organic polyhalogen compound-1 dispersion was obtained. Particles of the organic polyhalogen compound included in thus resulting polyhalogen compound dispersion had a median diameter of 0.41 µm, and a maximum particle diameter of 2.0 µm or less. The resultant organic polyhalogen compound dispersion was subjected to filtration with a polypropylene filter having a pore size of 10.0 µm to remove foreign substances such as dust, and was stored.

[0229]

<<Preparation of Organic Polyhalogen Compound-2 Dispersion>>

An organic polyhalogen compound-2 (N-butyl-3-tribromomethane sulfonylbenzoamide) in an amount of 10 kg, 20 kg of a 10% by mass aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP203) and 0.4 kg of a 20% by mass aqueous solution of sodium triisopropylnaphthalenesulfonate were added, and thoroughly admixed to give slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.) packed with zirconia beads having the mean particle diameter of 0.5 mm for 5 hours. Thereafter, 0.2 g of a benzoisothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the organic polyhalogen compound to be 30% by mass. This fluid dispersion was heated at 40°C for 5 hours to obtain an organic polyhalogen compound-2 dispersion. Particles of the organic polyhalogen compound included in thus resulting polyhalogen compound dispersion had a median diameter of 0.40 µm, and a maximum particle diameter of 1.3 µm or less. The resultant organic polyhalogen compound dispersion was subjected to filtration with a polypropylene filter having a pore size of 3.0 µm to remove foreign substances such as dust, and was stored.

[0230]

7) Preparation of Phthalazine Compound-1 Solution

Modified polyvinyl alcohol MP203 manufactured by Kuraray Co., Ltd., in an amount of 8 kg was dissolved in 174.57 kg of water, and then thereto were added 3.15 kg of a 20% by mass aqueous solution of sodium triisopropylnaphthalenesulfonate and 14.28 kg of a 70% by mass aqueous solution of a phthalazine compound-1 (6-isopropyl phthalazine) to prepare a 5% by mass phthalazine compound-1 solution.

[0231]

8) Preparation of an Aqueous Solution of Mercapto Compound-1

A mercapto compound-1 (1-(3-methylureido)-5-mercaptotetrazole) in an amount of 20 g was dissolved in 980 g of water to give a 2.0% by mass aqueous solution.

[0232]

9) Preparation of Solution of Benzotriazole Compound-1

20 g of Benzotriazole Compound-1 (1-1) was dissolved in 1980 g of methanol to obtain a 1.0% by mass solution.

[0233]

10) Preparation of Pigment-1 Dispersion

C.I. Pigment Blue 60 in an amount of 64 g and 6.4 g of DEMOL N manufactured by Kao Corporation were added to 250 g water and thoroughly mixed to give slurry. Zirconia beads having the mean particle diameter of 0.5 mm were provided in an amount of 800 g, and charged in a vessel with the slurry. Dispersion was performed with a dispersing machine (1/4G sand grinder mill: manufactured by IMEX Co., Ltd.) for 25 hours. Thereto was added water to adjust so that the concentration of the pigment became 5% by mass to obtain a pigment-1 dispersion. Particles of the pigment included in thus resulting pigment dispersion had a mean particle diameter of 0.21 µm.

[0234]

11) Preparation of SBR Latex Solution

SBR latex was prepared as described below.

To a polymerization tank of a gas monomer reaction apparatus (manufactured by Taiatsu Techno Corporation, TAS-2J type), were charged 287 g of distilled water, 7.73 g of a surfactant (Pionin A-43-S (manufactured by TAKEMOTO OIL & FAT CO.,LTD.): solid matter content of 48.5% by weight), 14.06 mL of 1 mol/liter NaOH, 0.15 g of ethylenediamine tetraacetate tetrasodium salt, 255 g of styrene, 11.25 g of acrylic acid, and 3.0 g of tert-dodecyl mercaptan, followed by sealing of the reaction vessel and stirring at a stirring rate of 200 rpm. Degassing was conducted with a vacuum pump, followed by repeating nitrogen gas replacement several times. Thereinto was injected 108.75 g of 1,3-butadiene, and the inner temperature was elevated to 60°C. Thereto was added a solution of 1.875 g of ammonium persulfate dissolved in 50 mL of water, and the mixture was stirred for 5 hours as it stood. The temperature was further elevated to 90°C, followed by stirring for 3 hours. After completing the reaction, the inner temperature was lowered to reach the room temperature, and thereafter the mixture was treated by adding 1 mol/liter NaOH and NH₄OH to give the molar ration of Na⁺ ion : NH₄⁺ ion = 1 : 5.3, and thus, the pH of the mixture was adjusted to 8.4. Thereafter, filtration with a polypropylene filter having the pore size of 1.0 μm was conducted to remove foreign substances such as dust followed by storage. Accordingly, SBR latex was obtained in an amount of 774.7 g. Upon the measurement of halogen ion by ion chromatography, concentration of chloride ion was revealed to be 3 ppm. As a result of the measurement of the concentration of the chelating agent by high performance liquid chromatography, it was revealed to be 145 ppm.

[0235]

The aforementioned latex had the mean particle diameter of 90 nm, Tg of 17°C, solid matter concentration of 44% by mass, the equilibrium moisture content at 25°C, 60% RH of 0.6% by mass, ionic conductance of 4.80 mS/cm (measurement of the ionic conductance performed using a conductivity meter CM-30S manufactured by Toa Electronics Ltd. for the latex stock solution (44% by mass) at 25°C).

SBR latex solutions having different Tgs can be prepared in the same way by appropriately changing the proportion of butadiene.

[0236]

12) Preparation of Dispersion of Thermal Solvent

To 10 kg of a thermal solvent (stearic amide (melting point of 100°C)) and 16 kg of a 10% by mass aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP203) was added 10 kg of water, and thoroughly mixed to give slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.) packed with zirconia beads having the mean particle diameter of 0.5 mm for 4 hours and 30 minutes. Thereafter, 0.2 g of a benzoisothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the thermal solvent to be 22% by mass to obtain a thermal solvent dispersion. Time period for dispersion was regulated so that the median diameter became 0.45 μm. Accordingly, particles of the thermal solvent included in thus resulting hot melt agent dispersion had a median diameter of 0.45 μm, and a maximum particle diameter of 1.4 μm or less. The resultant hot melt agent dispersion was subjected to filtration with a polypropylene filter having a pore size of 3.0 μm to remove foreign substances such as dust.

[0237]

2. Preparation of Coating Solution

1) Preparation of Coating Solution for Image Forming Layer-1

The dispersion 1 of the silver salt of fatty acid obtained as described above in an amount of 1000 g, 135 mL of water, 36 g of the pigment-1 dispersion, 25 g of the organic polyhalogen compound-1 dispersion, 39 g of the organic polyhalogen compound-2 dispersion, 171 g of the phthalazine compound-1 solution, 1060 g of the SBR latex (Tg: 17°C) solution, 153 g of the reducing agent-1 dispersion, 55 g of the hydrogen bonding compound-1 dispersion, 4.8 g of the development accelerator-1 dispersion, 5.2 g of the development accelerator-2 dispersion, 2.1 g of the color-tone-adjusting agent-1 dispersion, 8 mL of the mercapto compound-2 aqueous solution, 8 mL of benzotriazole compound-1 solution, and 76 g of themal solvent dispersion were serially added. The coating solution for the image forming layer prepared by adding 140 g of the silver halide mixed emulsion A thereto followed by thorough mixing just prior to the coating was fed directly to a coating die and coated.

[0238]

2) Preparation of Coating Solution for Emulsion Surface-Side Intermediate Layer

To 1000 g of polyvinyl alcohol PVA-205 (manufactured by Kuraray Co., Ltd.), 163 g of the pigment-1 dispersion, 33g of an aqueous solution of a blue dye-1 (manufactured by Nippon Kayaku Co., Ltd.: Kayafect turquoise RN liquid 150), 27 mL of a 5% by mass aqueous solution of di(2-ethylhexyl) sodium sulfosuccinate and 4200 mL of a 19% by mass solution of methyl methacrylate/ styrene/ butyl acrylate/ hydroxyethyl methacrylate/ acrylic acid copolymer (weight ratio of the copolymerization of 57/ 8/ 28/ 5/ 2) latex, were added 27 mL of a 5% by mass aqueous solution of aerosol OT (manufactured by American Cyanamid Co.), 135 mL of a 20% by mass aqueous solution of ammonium secondary phthalate and water to give total amount of 10000 g. The mixture was adjusted with NaOH to give the pH of 7.5. Accordingly, the coating solution for the intermediate layer was prepared, and was fed to a coating die to provide 8.9 mL/m².

Viscosity of the coating solution was 58 [mPa·s] which was measured with a B type viscometer at 40°C (No. 1 rotor, 60 rpm).

[0239]

3) Preparation of Coating Solution for First Layer of Emulsion Surface-Side Surface Protective Layers

In 840 mL of water were dissolved 100 g of inert gelatin and 10 mg of benzoisothiazolinone, and thereto were added 180 g of a 19% by mass solution of methyl methacrylate/ styrene/ butyl acrylate/ hydroxyethyl methacrylate/ acrylic acid copolymer (weight ratio of the copolymerization of 57/ 8/ 28/ 5/ 2) latex, 46 mL of a 15% by mass methanol solution of phthalic acid and 5.4 mL of a 5% by mass aqueous solution of di(2-ethylhexyl) sodium sulfosuccinate, and were mixed. Immediately before coating, 40 mL of a 4% by mass chrome alum which had been mixed with a static mixer was fed to a coating die so that the amount of the coating solution became 26.1 mL/m².

Viscosity of the coating solution was 20 [mPa·s] which was measured with a B type viscometer at 40°C (No. 1 rotor, 60 rpm).

[0240]

4) Preparation of Coating Solution for Second Layer of Emulsion Surface-Side Surface Protective Layers

In 800 mL of water were dissolved 100 g of inert gelatin and 10 mg of

benzoisothiazolinone, and thereto were added 180 g of a 19% by mass solution of methyl methacrylate/ styrene/ butyl acrylate/ hydroxyethyl methacrylate/ acrylic acid copolymer (weight ratio of the copolymerization of 57/ 8/ 28/ 5/ 2) latex, 40 mL of a 15% by mass methanol solution of phthalic acid, 5.5 mL of a 1% by mass solution of a fluorocarbon surfactant (F-1), 5.5 mL of a 1% by mass aqueous solution of a fluorocarbon surfactant (F-2), 28 mL of a 5% by mass aqueous solution of di(2-ethylhexyl) sodium sulfosuccinate, 4 g of polymethyl methacrylate fine particles (mean particle diameter of 0.7 μm) and 21 g of polymethyl methacrylate fine particles (mean particle diameter of 4.5 μm), and were mixed to give a coating solution for the surface protective layer, which was fed to a coating die so that 8.3 mL/m^2 could be provided.

Viscosity of the coating solution was 19 [$\text{mPa}\cdot\text{s}$] which was measured with a B type viscometer at 40°C (No. 1 rotor, 60 rpm).

[0241]

3. Preparation of Photothermographic Material-1
1) Preparation of Photothermographic Material-1

The back surface side of the undercoated support was subjected to simultaneous double coating so that the coating solution for the antihalation layer gives the coating amount of gelatin of 0.52 g/m^2 , and so that the coating solution for the back surface protective layer gives the coating amount of gelatin of 1.7 g/m^2 , followed by drying to produce a back layer.

[0242]

Reverse surface of the back surface was subjected to simultaneous overlaying coating by a slide bead coating method in order of the image forming layer, intermediate layer, first layer of the protective layer and second layer of the protective layer starting from the undercoated face, and thus a sample of the photothermographic material was produced. In this method, the temperature of the coating solution was adjusted to 31°C for the image forming layer and intermediate layer, to 36°C for the first layer of the protective layer, and to 37°C for the second layer of the protective layer.

The coating amount of each compound for the image forming layer (g/m^2) is as follows.

[0243]

Silver behenate	5.27
Thermal solvent	0.35
Pigment (C. I. Pigment Blue 60)	0.036
Polyhalogen compound-1	0.14
Polyhalogen compound 2	0.28
Phthalazine compound-1	0.18
SBR latex	9.43
Reducing agent-2	0.77
Hydrogen bonding compound-1	0.28
Development accelerator-1	0.019
Development accelerator-2	0.016
Color-tone-adjusting agent-1	0.006
Mercapto compound-1	0.003
Benzotriazole compound-1	0.0015
Silver halide (on the basis of Ag content)	0.13

[0244]

Conditions for coating and drying are as follows.

Coating was performed at the speed of 160 m/min, with the clearance between the leading end of the coating die and the support being 0.10 mm to 0.30 mm, and with the pressure in the vacuum chamber set to be lower than atmospheric pressure by 196 Pa to 882 Pa. The support was discharged by ionic wind prior to coating.

In the subsequent cooling zone, the coating solution was cooled by wind having the dry-bulb temperature of 10 °C to 20°C. Thereafter, conveyance with no contact was carried out, and the coated support was dried with an air of the dry-bulb of 23 °C to 45°C and the wet-bulb of 15 °C to 21°C in a helical type contactless drying apparatus.

After drying, moisture conditioning was performed at 25°C in the humidity of 40% RH to 60% RH. Then, the film surface was heated to be 70°C to 90°C. After heating, the film surface was cooled to 25°C.

Thus prepared photothermographic material had the matness of 550 seconds on the image forming layer side surface, and 130 seconds on the back surface as Beck's smoothness. In addition, measurement of the pH of the film surface on the image forming layer side surface gave the result of 6.0.

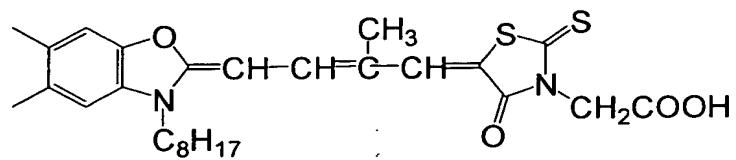
[0245]

Chemical structures of the compounds used in Examples of the invention are shown below.

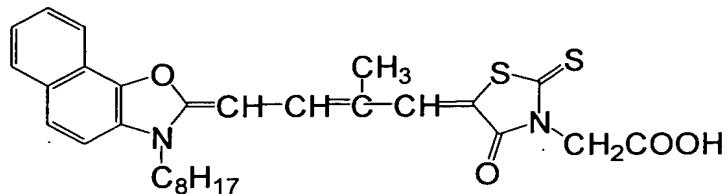
[0246]

[Formula 19]

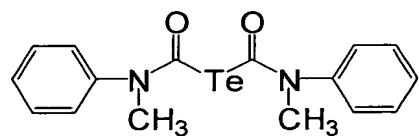
Spectral Sensitizing Dye A



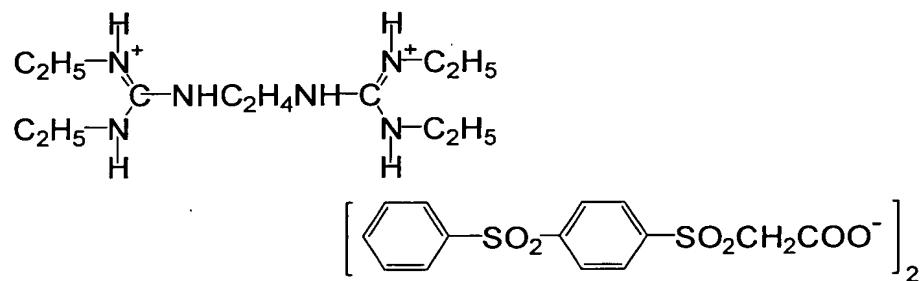
Spectral Sensitizing Dye B



Tellurium Sensitizer C

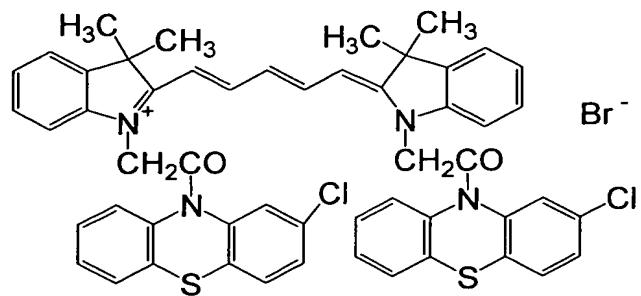


Base Precursor Compound-1

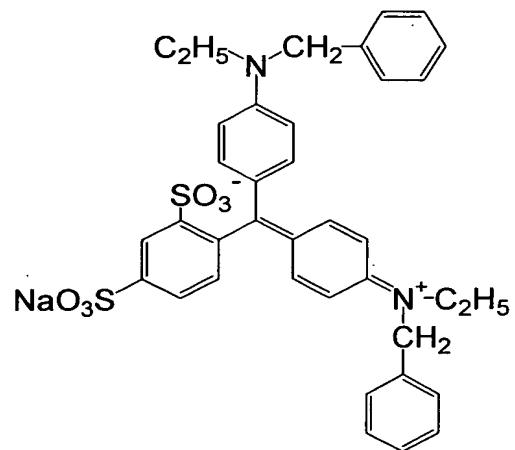


[0247]
[Formula 20]

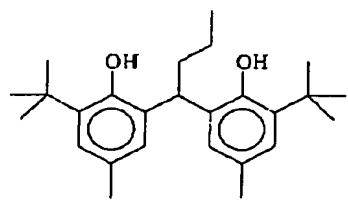
Cyanine Dye Compound-1



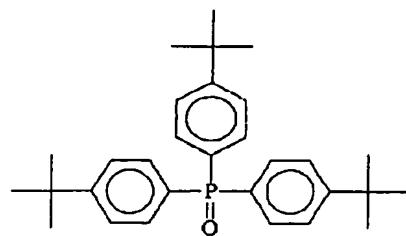
Blue Dye Compound-1



(Reducing Agent-1)

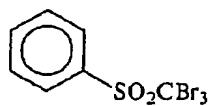


(Hydrogen-Bonding Compound-1)

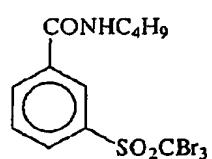


[0248]
[Formula 21]

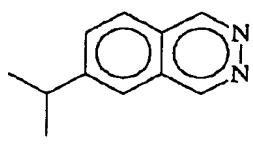
(Polyhalogen Compound-1)



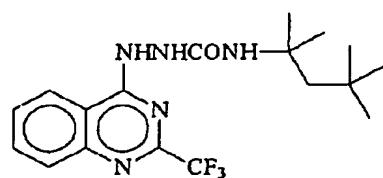
(Polyhalogen Compound-2)



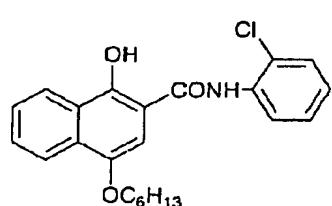
(Phthalazine Compound-1)



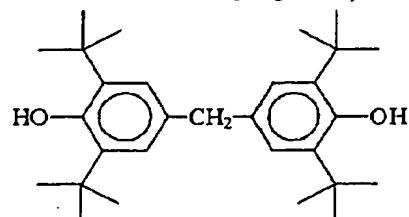
(Development Accelerator-1)



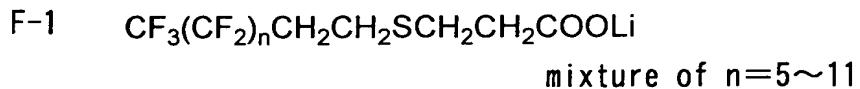
(Development Accelerator-2)



(Color-Tone-Adjusting Agent-1)



[0249]
[Formula 22]



[0250]
4. Evaluation of Photographic Performances
(Preparation)

The resulting sample was cut into a half-cut size (43 cm in length x 35 cm in width), and was cut at four corners. The sample was wrapped with the following packaging material under an environment of 25°C and 50% RH, and stored for 2 weeks at an ambient temperature.

(Packaging Material)

PET 10 µm/ PE 12 µm/ aluminum foil 9 µm/ Ny 15 µm/ polyethylene 50 µm containing carbon at 3% by weight, oxygen permeability: 0.02 mL/atm · m² · 25°C · day, vapor permeability: 0.10 g/atm · m² · 25°C · day.

[0251]
(Exposure and Development of Photothermographic Materials)

Exposure and thermal development (14 seconds in total with 3 panel heaters set to be 107°C - 121°C - 121°C) were performed with a laser imager (equipped with 660 nm semiconductor laser having the maximum output of 50 mW (IIIB)) described in Japanese Patent Application No. 2002-088832 and Japanese Patent Application No. 2002-091114.

Sample 1 was obtained by processing the sample with the processor in which the distance between the thermal development heating section and development discharging section was set to be 80 cm, and the transportation speed was 2.86 cm/second. Sample 2 was obtained by processing the sample with the processor in which the distance between the thermal development heating section and development discharging section was set to be 50 cm, and the transportation speed was 2.13 cm/second. Both of these samples were discharged within 35 seconds after heating for thermal development was finished.

[0252]
5. Results

According to both samples processed with the cooling time between the thermal development heating section and development discharging section being 35 seconds or less, the developed images were clear. From this result, the cooling time in the cooling section could be shortened, and increasing the speed of the process per one sheet of photothermographic material and reducing the size of the image recording apparatus were improved.

[0253]
Example 2
<<Preparations of Dispersion of Silver Salt of Fatty Acid 2 to 4>>

Preparations of dispersion of silver salt of fatty acid 2 to 4 were conducted in the similar manner to that of dispersion of silver salt of fatty acid 1 except that fatty acids

(behenic acid, stearic acid, lignoceric acid and arachidic acid) with a ratio presented in Table 11 were used instead of behenic acid (Henkel Co.).

[0254]
[Table 1]

Silver salt of fatty acid dispersion	Fatty acid composition (mol%)			
	behenic acid	lignoceric acid	arachidic acid	stearic acid
1	96	2	2	0
2	75	5	10	10
3	40	5	25	30
4	15	5	40	40

[0255]
<< Preparation of Dispersions of Reducing Agent-2 to -5 >>
Preparation of dispersions of reducing agent-2 to -5 was conducted similarly to Example 1 except that reducing agents shown in Table 3 were used.
Preparation of dispersions of development accelerator-3 to -5 was conducted similarly to Example 1 except that development accelerators shown in Table 3 were used.
Preparation of dispersions of thermal solvent-2 and -3 was conducted similarly to Example 1 except that thermal solvents shown in Table 3 were used.

[0256]
<<Preparation of Coating Solutions for Image Forming Layer-2 to -14>>
Preparation of coating solution for image forming layer-2 to -14 was conducted in the similar manner to the preparation of coating solution for image forming layer-1, except that dispersion of silver salt of fatty acid, reducing agent dispersion, dispersion of development accelerator and thermal solvent dispersion were changed as shown in Table 3.

[0257]
<<Preparation of Photothermographic Material-2 to -14>>
Preparation of photothermographic material-2 to -14 was conducted in the similar manner to the preparation of photothermographic material-1, except that the coating solutions for image forming layer-2 to -14 were used instead of the coating solution for image forming layer-1 used in the preparation of the photothermographic material-1.

[0258]
(Exposure and Development of Photothermographic Materials)
Exposure and thermal development (14 seconds in total with 3 panel heaters set to be 107°C - 121°C - 121°C) were performed with a laser imager (equipped with 660 nm semiconductor laser having the maximum output of 50 mW (IIIB)) described in Japanese Patent Application No. 2002-088832 and Japanese Patent Application No. 2002-091114. The exposure value was detected to make the image density of 1.0 by a thermal development of 14 seconds. The exposure was performed with that exposure value, followed by a thermal development of 16 seconds, and the optical density of the image was measured. The distance between the thermal development heating section and development discharging section was 57 cm, and the transportation speed at this space was 2.86 cm/second. The time (cooling time) at this space was 23.9 seconds.

[0259]

(Evaluation of Photographic Properties)

The photothermographic materials described above were evaluated as follows.

1. Evaluation of Unevenness of Image Density

The samples cut in the half-cut size (43 cm in length x 35 cm in width) were exposed to give uniform images and 5 sheets of them were developed continuously. The density of the center of the sheet was measured by a densitometer. Among the 5 sheets, the difference between the highest and the lowest value in the density is defined as ΔD . The smaller ΔD is, the more preferable it is, because it means that the stable image is given.

[0260]

2. Evaluation of Fog

Evaluation of unexposed parts of the photosensitive material was carried out with Macbeth TD904 densitometer (visible density). Results of the measurement were evaluated for the minimal density, D_{min} (fog).

[Table 2]

Photothermographic material	Content of silver behenate (mol%)	Reducing agent	Development accelerator	Thermal solvent	Density at development time of 14sec	Density at development time of 16sec	Fog (Dmin)	Density difference (ΔD)	Remarks
2	96	R-4	A-1/A-8	—	1.0	1.26	0.20	0.16	Present invention
3	75	R-4	A-1/A-8	—	1.0	1.25	0.22	0.16	Present invention
4	40	R-4	A-1/A-8	—	1.0	1.27	0.26	0.20	Present invention
5	15	R-4	A-1/A-8	—	1.0	1.28	0.30	0.27	Present invention
6	96	R-3	A-1/A-8	—	1.0	1.1	0.22	0.10	Present invention
7	96	R-18	A-1/A-8	—	1.0	1.07	0.21	0.05	Present invention
8	96	R-5	A-1/A-8	—	1.0	1.05	0.20	0.09	Present invention
9	96	R-6	A-1/A-8	—	1.0	1.12	0.23	0.08	Present invention
10	96	R-4	—	—	1.0	1.28	0.22	0.16	Present invention
11	96	R-4	A-1	—	1.0	1.25	0.20	0.18	Present invention
12	96	R-4	A-8	—	1.0	1.26	0.21	0.16	Present invention
13	96	R-4	A-1/A-8	stearic amide	1.0	1.11	0.24	0.11	Present invention
14	96	R-4	A-1/A-8	Salicyl anilide	1.0	1.16	0.24	0.12	Present invention

[0261]

As shown in Table 2, it was possible to output the image in the image forming method wherein the cooling time is 35 seconds or less, and further, a stable output image was obtained by using photothermographic material which gives the image density 1.0 to 1.3 (in the condition that exposure was carried out with the exposure value to make the image density of 1.0 by a thermal development of 14 seconds, and thermal development was carried out for 16 seconds). Especially, a stable output image was obtained by using organic silver salt containing 30 mol% to 100 mol% silver behenate, adding development accelerator and using reducing agent described by general formula (R) (especially the reducing agent where the R¹¹ and R^{11'} in the formula each independently represent an secondary or tertiary alkyl group having 3 to 15 carbon atoms).

[0262]

Example 3

<<Preparation of Benzotriazole Compound-2 Aqueous Solution>>

Preparation of a benzotriazole compound-2 solution was conducted in the similar manner to the preparation of benzotriazole compound-1 aqueous solution in Example 1, except that benzotriazole compound-2 (2-2) was used instead of the benzotriazole compound-1.

<<Preparation of Coating Solutions for Image Forming Layer-15 to -17>>

Preparation of coating solutions for image forming layer-15 to -17 was conducted in the similar manner to the preparation of the coating solution for image forming layer-1 except that mercapto compound and benzotriazole compound were changed to the compounds shown in Table 3.

[0263]

<<Preparation of Photothermographic Material-15 to -17>>

Preparation of photothermographic material-15 to -17 was conducted in the similar manner to the preparation of the photothermographic material-1 except that the above-mentioned coating solutions for image forming layer-15 to -17 were used instead of the coating solution for image forming layer-1.

[0264]

Evaluations of the above-mentioned photothermographic material-15 to -17 were carried out similarly to Example 2.

[Table 3]

Photothermographic material	Mercapto compound	Benzotriazole compound	Density at development time of 14sec	Density at development time of 16sec	Fog	Density difference (ΔD)	Remarks
1	-1	-1	1.0	1.26	0.20	0.16	Present invention
15	—	-1	1.0	1.28	0.44	0.18	Present invention
16	-1	—	1.0	1.28	0.32	0.20	Present invention
17	-1	-2	1.0	1.25	0.17	0.15	Present invention

As shown in Table 3, the fog value was lowered by adding mercapto compound and

benzotriazole compound even though the cooling time was short like 35 seconds or less.

[0265]

Example 4

<<Preparation of Phthalazine Compound-2 and -3 Solutions>>

Preparation of phthalazine compound-2 and -3 solutions was conducted similarly to preparation of phthalazine compound-1 solution in Example 1 except that the amount of the phthalazine compound-1 added was changed as shown in Table 4.

<<Preparations of Coating Solutions for Image Forming Layer-18 to -20>>

Preparation of coating solutions for image forming layer-18 to -20 was conducted in the similar manner to the preparation of the coating solution for image forming layer-1 except that the application amount of phthalazine compound was changed as shown in Table 4.

[0266]

<<Preparations of Photothermographic Material-18 to -20>>

Preparation of photothermographic material-18 to -20 was conducted in the similar manner to the preparation of photothermographic material-1 except that the above-mentioned coating solutions for image forming layer-18 to -20 were used instead of the coating solution for image forming layer-1.

[0267]

Evaluations of above-mentioned photothermographic material-118 to -120 were carried out similar to Example 12.

[Table 4]

Photothermographic material	Phthalazine compound	Addition amount of phthalazine compound	Density at development time 14sec	Density at development time 16sec	fog	Density difference ΔD	Remarks
1	-1	0.18	1.0	1.26	0.20	0.16	Present invention
18	-1	0.14	1.0	1.29	0.21	0.27	Present invention
19	-1	0.16	1.0	1.26	0.20	0.16	Present invention
20	-1	0.2	1.0	1.2	0.22	0.10	Present invention

As shown in Table 4, the developed image was more stable and the density between the photothermographic materials was uniform when the amount of phthalazine compound was increased even though the cooling time was short like 35 seconds or less.

[0268]

[Effects of the Invention]

According to the invention, there can be provided an image forming method using a photothermographic material which can output images even in a developing device with short image processing time.

[BRIEF DESCRIPTION OF THE DRAWING]

[Fig. 1]

Fig. 1 is a schematic view of a thermal developing recording device including a laser

recording device according to the present invention.

[Description of the Reference Numerals]

- 3: photothermographic recording material
- 10a, 10b, 10c: trays for photosensitive materials
- 13a, 13b, 13c: sheet conveyor rollers
- 15a, 15b, 15c: photosensitive materials
- 16: upper light-shielding cover
- 17: conveying section for sub-scanning (sub-scanning means)
- 19: scanning-exposing section (laser irradiation means)
- 51a, 51b, 51c: thermal developing plates
- 52: driving roller
- 53: reduction gear
- 55: opposing roller for conveyance
- 57: cooling rotor
- 59: cooling rotor
- 61: cooling plate
- 63: discharging rollers
- 100: laser recording device
- 150: thermal developing recording device

[DOCUMENT NAME] DRAWING
[FIG. 1]

